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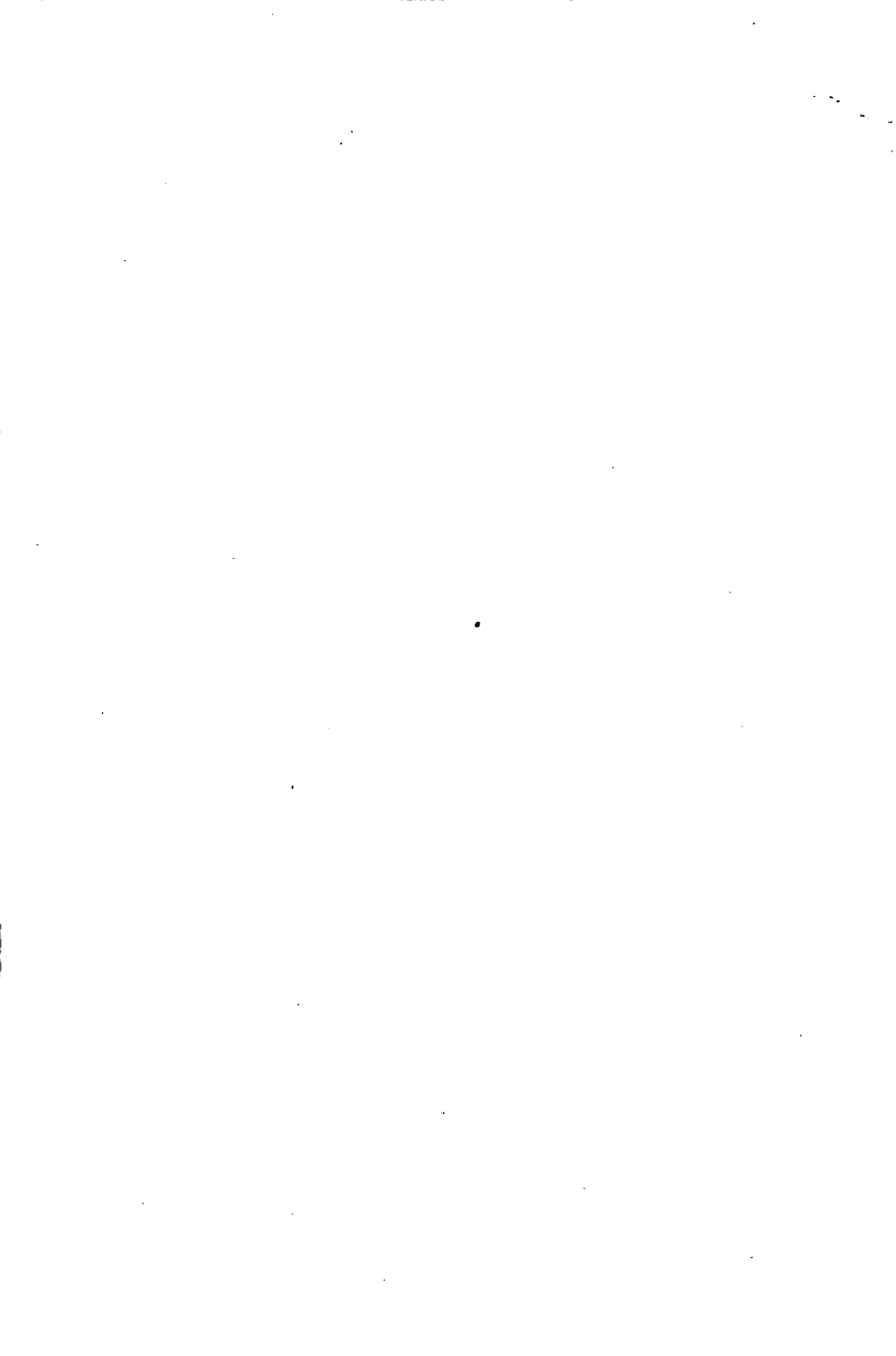
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Frontispiece

**REMOVAL OF GAMBOA DIKE IN THE PANAMA CANAL
A TRIUMPH OF CHEMISTRY OVER NATURAL OBSTACLES**

Through the scientific skill of the chemist a great storehouse of energy can be concentrated in dynamite and there remain quiescent until it is called into action in the right location and at the desired moment.

FOUNDATIONS OF CHEMISTRY

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PREFACE

FORMERLY, the study of the classics occupied a very prominent position in educational training, and many of the ablest men of our times owe their efficiency largely to the excellence of the mental discipline thus acquired. The essential mental training can, however, be furnished in the study of subjects that possess vital interest and present-day usefulness, provided these subjects are as well taught as were the classics.

A tendency is now evident in secondary school education to depart from the study of the classics and to substitute therefor a multitude of vocational and informational subjects. It is extremely likely that this type of study will not only fail to prove as practically useful as its advocates hope, but that it will fail to impart that sturdy independence of thinking—that ability to apply what has previously been gained—which is so essential to success in all walks of life, and which can be imparted in large measure by a thorough study of the underlying principles of science in their applications to well-selected cases.

With the ideal in mind of teaching the scientific method of thought while considering the facts and principles of chemistry, the authors have striven to write a book the intelligent study of which will develop both the power of the pupil to think originally and his appreciation of the relation between the subject matter of chemistry and his daily life.

In illustrating the principles of chemistry, very many important industrial processes and applications to daily

life have been chosen, but the greatest effort has been made to keep the idea uppermost that the principles concerned are of universal application, whereas the individual processes are transient and of relatively less importance to the general student of chemistry.

In the development of the subject, the plan has been to proceed from simple and well-known facts to others less familiar. The consideration of chemical theory is deferred to later chapters so that a good basis of fact may have accumulated before the theory arising from the facts is considered.

The problems at the end of the chapters are graded in difficulty and some are designed to tax the thinking powers of the brightest students, for it is true that a course in science to be of greatest value must inspire the pupil to think. The instructor may find it wise in some cases to select from the list of questions those which best meet the needs of his own students.

In the opinion of the authors, the first twenty-four chapters include as much ground as can be thoroughly covered by the average high school pupil in a year. The subject matter of the remaining chapters is, on the whole, more difficult, and a more advanced method of treatment has been used in order that more mature classes may continue to receive mental stimulus from the work.

In conclusion, the authors find it a pleasant duty to acknowledge encouragement and assistance received from many of their friends.

The chapters relating to food chemistry have been read by Professor A. G. Woodman and the chapters on the carbon compounds by Professor F. J. Moore, both of the Massachusetts Institute of Technology, and both of these gentlemen have offered many helpful suggestions. The

chapter on Metallurgy has been written in collaboration with Professor Carle R. Hayward, of the Department of Mining and Metallurgy of the Massachusetts Institute of Technology. The entire manuscript has been read by Professors J. W. Phelan and Edward Mueller, of the Massachusetts Institute of Technology.

Mr. Charles J. Pieper, of the University High School, Chicago, Miss Ellinor Garber, Mr. Mont K. Baird, and Mr. E. Vernon Hahn, of the Shortridge High School, Indianapolis, have made many valuable suggestions. Photographs for illustrations have been furnished by: The Solvay Process Company, W. B. Scaife and Sons Company, The Carborundum Company, The Goldschmidt Thermit Company, the Loomis-Pettibone Company, and The American Museum of Natural History.

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FOUNDATIONS OF CHEMISTRY

CHAPTER I

CHEMICAL AND PHYSICAL CHANGES

CHEMISTRY is the science which deals with the substances which go to make up our earth and everything in the earth, — sea, atmosphere, rocks, plants, and animals. Chemistry is little interested in the size or shape of bodies of matter, its concern is with the substances of which the bodies are composed. For example, a large irregular ledge of marble is marble, and is to the chemist the same substance as the marble of the most beautifully chiseled statue. To a sculptor or an architect the size and form of a marble block are of supreme importance; but to the chemist it is the substance that is of importance. To a zoölogist the difference between two kinds of animals, for example between a rabbit and an elephant, is most marked; to a chemist, on the other hand, the differences are of small importance, since both creatures are built up of practically the same chemical substances, and the life of both is dependent on the same kind of chemical processes.

Substances are continually undergoing change, as when coal burns or wood decays or the food of animals is digested; and all such changes of substances come within the scope of chemistry. Mere changes in size and form, as when a block of marble is chiseled or a band of rubber is stretched, have no place in the study of chemistry, because there is no change of substance.

1. A Typical Chemical Substance: Charcoal. Let us examine a familiar substance, charcoal. Because ordinary wood charcoal contains impurities, it is better for us to consider a very pure form of charcoal, which may easily be made by charring sugar.

Charcoal is black, porous, light in weight, brittle, and easily crushed to a powder. These are some of the *physical properties* of charcoal and they are inherent in charcoal. It is by observing these properties that we are enabled to distinguish it from other substances; for example, from marble.

When charcoal burns, it undergoes a great change and thereby loses all of these physical properties. The fact that it can burn when in contact with air constitutes one of the *chemical properties* of charcoal.

2. A Typical Chemical Change. Let us place a layer of sugar charcoal upon a grate so that air may have free access to it, and heat the lower part of the layer until it begins to glow; in other words, let us set fire to it. As we continue to observe the charcoal after removing the source of heat, we note that it does not become cool again, but that the heat persists, and even grows stronger, and the glow spreads throughout the whole layer. We note that the bulk of the charcoal is diminishing, and at length we find that it has entirely disappeared. When ordinary wood charcoal is burned, a small quantity of white ashes is left, otherwise its behavior is exactly the same.

What now is the real nature of this change? Has the charcoal been destroyed? We can certainly no longer see it or feel it, but this does not necessarily mean that it has ceased to exist as matter. Many well-known forms of matter are imperceptible so far as our most-used means of observation go. For example, when we look through a pane of very

clear glass or a layer of very clear water, we can hardly detect these materials in our line of vision. We live at the bottom of a sea of air, of the presence of which we have abundant evidence in the wind and in such facts as our ability to use it to inflate automobile tires. Moreover, it has been found by scientific men to be an invariable rule of nature that matter is never destroyed. This rule is known as the *law of the conservation of matter*. *Matter may change its form, but its quantity, which is measured by its weight, never increases or decreases.*

If we accept the experience of scientific men as proof of the correctness of this law, we must conclude that the charcoal has not ceased to exist, but has merely changed to or become part of a substance which, like air, is invisible. In point of fact this conclusion is correct. The substance produced by burning the charcoal has many properties by which its presence may be ascertained. One of its most characteristic properties is that it is absorbed by limewater, and thereby at once renders the latter milky in appearance. This is a property not possessed by air or by charcoal. If this product of burning charcoal is collected and weighed, it is found to weigh three and a half times as much as the original charcoal.

Assuming again the correctness of the law of the conservation of matter, which states also that the quantity of matter does not increase, we must conclude that this gas that is formed cannot be composed alone of the same matter as the charcoal, but that something must have been added to that substance. This added substance must have come from the air. It is in fact what we call *oxygen*, and the new substance formed by its action with the charcoal is called *carbon dioxide*.

That something from the air is essential in the production of the new substance is all the more strikingly shown if the charcoal is heated out of contact with the air; as, for example, in a vacuum, that is, in a closed vessel out of which the air has been pumped. When the charcoal is again allowed to cool after this heating, it recovers its original appearance and is found to have neither lost nor gained in weight.

Let us sum up the facts already stated concerning the behavior of charcoal and air. When charcoal burns in air, the charcoal ceases to exist as charcoal, but it and something from the air form a new substance, which has properties different from those of either of the original substances. Accompanying this change in the kind of substance, a large amount of heat is developed.

3. Characteristics of a Chemical Change. In the example which we have been considering we have illustrated some of the important characteristics of chemical changes, and we should now be able to recognize a case of chemical change by observing these characteristics. *The substances present in the beginning lose their properties and are changed into new substances with radically different properties. In general, heat effects accompany chemical changes and these effects are usually very marked when the change takes place rapidly.* The heat may be less intense, however, than in the case of the burning charcoal. Some chemical changes absorb heat rather than give it off.

4. Examples of Chemical Change. All other cases of burning are examples of chemical change; for in all such cases — whatever the fuel that is burnt — new substances with new properties are formed and the old substances disappear. Moreover the change is accompanied by the active giving forth of heat. The explosion of gunpowder

and of dynamite (see frontispiece) are also instances of chemical change.

The rusting of iron, the souring of milk, the decaying of wood, and the digestion of food in the body may be mentioned as other familiar cases of chemical change. In these latter cases the rate of change is slower than in burning and the heat effects are not so apparent. Nevertheless, it is true that the animal body is kept warm by the chemical changes which the food undergoes.

5. Physical Change. We observe changes of some of the properties when a block of marble is broken into fragments, or a steel spring is compressed, or the filament of an incandescent electric lamp is heated to white heat by the current, or gold is melted, or water is vaporized over a fire or is frozen on a cold day. But the steel spring returns to its original shape when it is released; on turning off the current, the incandescent filament again grows cold and black; on cooling, the melted gold resolidifies and the water vapor condenses to liquid water; and, on returning to the original temperature, the ice again turns to water. The fragments of the shattered block of marble, it is true, do not reunite into one solid piece, but this is not essential, because each of the fragments is recognized at once as marble, since it possesses the properties of marble and differs only in size and shape from the original block.

Such changes involve no change in the chemical nature of the substances and they are known as *physical changes*.

In our study of chemistry we shall have frequent occasion to distinguish between chemical and physical changes, and in most cases it is a very simple matter to make the distinction. There are, however, cases on the border line concerning which even scientists fail to agree.

SUMMARY

Chemistry is the science which deals with *substances* and the changes which substances undergo and are capable of undergoing.

A chemical change takes place when a substance, or substances, undergoes a change into a new substance, or substances, with widely different properties. Chemical changes usually involve the production of or the absorption of a large amount of heat. The burning of charcoal is one of the best known and most typical of chemical changes.

Conservation of Matter: *The amount of matter in the universe is constant; matter is not created or destroyed.* This statement is known as the law of the conservation of matter.

Physical changes are those in which bodies of substance are changed in any way without being altered in their chemical nature.

Questions

1. How are different chemical substances distinguished?
2. State three ways in which chemical changes differ from physical changes.
3. Give five examples of physical change.
4. Give five examples of chemical change. State what distinguishes each of these as a chemical rather than a physical change.
5. Mention three instances of chemical change in which the heat effect is so intense as to cause emission of light.
6. Mention three instances in which the heat effect is easily noticeable, but still not intense enough to produce a glow.
7. Mention three instances in which the heat effect is so slight that it is unnoticeable.
8. We may accept it as a reasonable supposition that just as much heat would be produced by the complete decay of a piece of wood as if the wood were to be burned. How do you explain the fact that the heat is very intense in only one of these cases?
9. Name the products of burning coal in a furnace. Is the chemical reaction carried on to obtain these new substances?
10. When a mason slakes lime to make mortar, is he interested in the heat produced?

CHAPTER II

MIXTURES AND CHEMICAL SUBSTANCES

6. Mixtures. Many, in fact most, of the bodies of matter familiar to us in everyday life are mixtures. Salt water, for example, is a mixture containing water and salt. A glass of salt water appears as clear as ordinary pure water, and it is impossible to see any separation into individual grains of salt or drops of water. Yet we know that we can make salt water by dissolving salt in water.

Granite, which is a well-known building stone, is also a mixture, — usually of three substances, quartz, feldspar, and mica; but in granite the separate particles of these substances are large enough to be easily seen.

Ordinary garden soil is a very complex mixture, containing sand, particles of decaying leaves, water, and various salts such as potassium nitrate, potassium carbonate, and calcium phosphate. The ingredients of the soil are so thoroughly mixed that they cannot be identified with the naked eye.

Many of the materials which are brought to the practical chemist for “analysis” are very complicated mixtures, and the work of the chemist frequently consists in finding out what substances are present in the mixtures and usually also what quantity of each substance. This he is able to do because he has been trained to know pure substances by their properties and has learned to use systematic methods of separating these substances.

7. Chemical Substances. Any kind of matter which is not a mixture is a *chemical substance*. Salt, sugar, sulphur, and carbon (charcoal) are examples of chemical substances, and none of these can be produced like salt water or garden soil by the mere putting together of different ingredients.

A chemical substance is uniform throughout its mass. Thus if we break a piece of any one of the above-mentioned substances into countless small pieces and examine each of these pieces by any means at our disposal, we find that each of the minute particles has just the same properties, except those of size and shape, as all the other pieces or as the unbroken lump.

But mere uniformity throughout the mass of a body of matter does not necessarily show that it is a single substance, for some mixtures, like salt water, are as uniform as the substances, salt, sugar, sulphur, and charcoal. Yet we know that we can prepare salt water by mixing; we find furthermore that we are able to separate salt water, as well as other mixtures, by rather simple processes, a few of which are outlined in the next section.

8. Methods of separating mixtures into their components are based on some physical property by which the components differ markedly from each other. Thus a component may be attracted to a magnet and the other components not; a component may be very volatile or very soluble or very heavy. Methods of separation are as varied as physical properties are varied, but we shall describe only a few practical methods of separating some typical mixtures.

A block of granite might be crushed, and then with the aid of a magnifying glass and delicate forceps the separate particles of quartz, feldspar, and mica might be picked out and laid in separate piles. This method, which may be

called *simple mechanical separation*, would, however, prove very wearisome.

Salt water is a mixture of so intimate a character that the most powerful microscope fails to show any separate particles of salt and of water, yet this mixture may be separated by distilling. The salt water is placed in a flask and boiled; the water changes into a vapor, steam, which passes off and may be led through a condenser, that is, a pipe surrounded by a cooling bath. Here the steam condenses to water which drips from the lower end of the condenser tube (see Fig. 1). The salt, which is not volatile, is left behind in the flask as a mass of crystals. This method of *distillation* has a very wide practical use for separat-

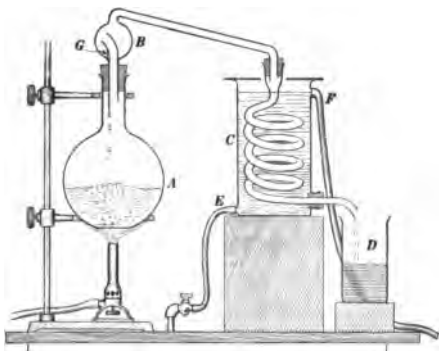


FIG. 1. — Distilling Apparatus. A, flask in which liquid is boiled. B, trap to catch spray from boiling liquid and prevent any non-volatile matter passing over with the vapor. C, condenser. D, receiver. E, cooling water enters from tap. F, overflow. G, opening through which liquid returns to flask.

ing mixtures of volatile and non-volatile substances, or even for separating substances of different degrees of volatility.

A mixture of sugar and sand can be separated if it is stirred up with water; the sugar dissolves in the water, while the sand remains unchanged. By pouring off the solution of sugar from the sand one accomplishes the separation. The solution may be made to give up its sugar if the water is evaporated away, just as the salt water gave up its salt on distillation. Here separation is accomplished by taking

advantage of *differences in solubility*. Such separations are carried out on an enormous scale in practical work.

A mixture of light and heavy particles, as, for example, a mixture of powdered sulphur and iron filings, may be separated by taking advantage of *differences in density*. Neither of these substances dissolves in water; but if the mixture is stirred vigorously with a large amount of water, the whole becomes suspended in the liquid. If the liquid is then left a moment at rest, the particles of iron, being heavy, settle rapidly to the bottom, while the lighter particles of sulphur remain suspended for a longer time. Then if the upper part of the liquid is poured off at the right moment, most of the suspended sulphur is carried with it, whereas the iron is left behind. If this process be carried out with sufficient care, the sulphur can be completely separated from the iron.

This type of separation is frequently made use of in industrial and mining operations that are carried out on a large scale. Most interesting perhaps is the separation of gold dust from gold-bearing sand.

9. Chemical Substances that can be separated. As already said above, a chemical substance is a material which cannot be prepared by the mere mixing of different ingredients, nor can it be separated by non-chemical means into different kinds of matter. Now the great majority of chemical substances, for example salt and sugar, *can be separated chemically* into two or more different substances, but the chemical means that must be employed to do this are very unlike the methods described under the last heading. To break down a chemical substance into different substances generally involves the expenditure of a large amount of energy, perhaps in the form of intense heat, perhaps in the

form of an electric current, and perhaps as chemical energy through interaction with some other chemical substance.

Furthermore, when a pure substance is separated chemically, the new substances are totally different in their properties from the original substance; whereas when a mixture is separated, each of the components still possesses the same properties which it showed in the mixture.

SUMMARY

A mixture is composed of two or more chemical substances. A coarse-grained mixture may be laboriously separated into its components by sorting out the particles by hand. More intimate mixtures may be separated by taking advantage of differences in the physical properties of the components, as, for example, differences in volatility, solubility, or density.

A pure chemical substance consists of a single kind of matter. If a pure substance is capable of being separated chemically into different substances, it is only by a process totally different from the methods of physical separation of mixtures; moreover the separation yields totally new substances with altogether new properties.

Questions

1. Look up in the dictionary the words *matter*, *substance*, *mixture*, *body*, *object*, and decide which of the meanings applies in chemistry.
2. Distinguish between the popular meaning of the word *substance* and the scientific meaning of the term *pure substance*.
3. Make use of the terms *substance*, *mixture*, *body*, and *object* in classifying the following: rain water, sea water, the Atlantic Ocean, Lake Superior, the block of ice that the ice man just delivered, sugar, maple sugar, hash, a mince pie, the marble statue in front of the city library, the ledge of marble on the mountain, iron, the old cannon in the museum.
4. How could the property of magnetism be used to separate a mixture of iron filings and powdered sulphur?
5. How could salt be separated from sand?

CHAPTER III

ELEMENTS AND COMPOUNDS

10. Elements. Of the substances of which we have spoken in the previous chapter, some — namely, sulphur, charcoal, and iron — cannot be separated into other than just the single substances by any means known to us, either by physical or by chemical processes. Such substances are known as elements; and up to the present day about eighty of these elementary substances have been discovered (see table inside the back cover).

The elements may combine chemically with other elements and thereby form totally different substances, but the elements can always be separated again undiminished in weight from the compounds. For example, if one kilogram of charcoal burns, although the charcoal disappears, there is still one kilogram of carbon in the carbon dioxide which is formed. (Carbon is the name of the element of which the substance charcoal consists. The element is always carbon, whatever the form or state of chemical combination; charcoal is a form of the uncombined element.) The carbon dioxide which escapes into the air is taken up mostly by trees and plants, where the element undergoes further chemical change, and thus this kilogram of carbon may eventually become part of the wood of trees. The wood may be charred again, and thus some at least of the original charcoal will return again to the form of charcoal.

Whatever the final form of the one kilogram of carbon, it still exists somewhere unchanged in weight.

We are perhaps not warranted in claiming with certainty that the elements are absolutely the simplest forms of matter. All that the chemist means to imply, when he calls a substance an element, is that it is something which human skill has been unable to resolve into two or more different substances.¹ In the past men have regarded as elements many substances which have since been shown to be separable.

One of the early attempts to classify substances was that of the ancient Greek philosophers, under the leadership of Aristotle, who divided all substances into four supposed elements, — earth, air, fire, and water. This division was based on fanciful speculation instead of scientific knowledge; but within recent times, even within a few decades, what have been supposed to be elements have in a few instances been found to be really mixtures of two or more elements.

11. Chemical Compounds. The number of chemical substances which the chemist has discovered is almost countless. A few of them, as we have seen, are elements, but the great majority are compounds of two or more elements. Salt and sugar are chemical compounds, so also are water, baking soda, washing soda, and alum.

It must not be thought, however, that these compounds are any the less chemical substances than the elements car-

¹ Recent discoveries in connection with the study of radioactive elements such as radium have tended to show that some of the elements, perhaps all, are constantly undergoing changes, some being produced while others are being disintegrated. It may be that the agencies which have produced the elements are still at work. Even with the most rapidly changing element, however, any increase or decrease in quantity is so small that it is almost or quite beyond the range of detection with the chemical balance.

bon, sulphur, and iron, for compounds have just as characteristic properties as have the elements themselves, and these properties are lost altogether whenever the compounds are separated into their elements.

Another important characteristic of chemical compounds is that *they always contain exactly the same proportion by weight of their constituent elements*. This statement is known as the **law of definite proportions**. Mixtures, on the other hand, may contain variable proportions of their ingredients. We shall find in succeeding chapters that a knowledge of the definite proportions in which elements are united in compounds is a matter of the utmost importance in the development of chemical science.

12. Mixtures and Compounds. Let us try to make clear the difference between physical mixtures and chemical compounds by comparing the effect of merely mixing two chemical substances on the one hand and causing them to combine chemically on the other hand.

Mixing may be accomplished by merely shaking or stirring substances together if they are first very finely divided.

13. Mixture of Iron and Sulphur. A mixture which can readily be made in the laboratory is one of iron and sulphur. If the very finest powdered sulphur and an impalpably fine iron dust are thoroughly stirred together, a mixture is obtained which appears like a uniform gray powder; to discover any unevenness in its texture it is necessary to employ a powerful microscope. Still this mixture may be separated into sulphur and iron by the method described on page 18. Another convenient method by which it can be separated is to treat it with carbon disulphide, a liquid in which sulphur dissolves much as salt dissolves in water. The iron is left undissolved and may

be separated by pouring off the liquid, and the sulphur may be obtained from the solution by allowing the carbon disulphide to evaporate.

14. Compound of Iron and Sulphur. Now let us fill a test tube with some of this intimate mixture of sulphur and iron, and heat the mixture in one spot until it begins to glow. On removing the test tube from the flame the glow does not subside, but spreads to every part of the mixture, giving forth light and heat and thus furnishing abundant evidence that a vigorous change is taking place. After the whole mass has thus entered into this reaction and has afterward been allowed to cool, it is found that there remains a hard cake. If proper proportions of iron and of sulphur were used this cake may now be pulverized and stirred up with water, and we shall not find any lighter particles of sulphur which float off nor any heavier particles of iron which settle. Neither will it be possible to dissolve out sulphur by means of carbon disulphide and leave iron behind.

Here, again, a chemical reaction has occurred with the appearance of a good deal of heat and light energy. A new substance totally unlike either of the original substances has been formed, and this cannot now be separated into the two original substances by any of the comparatively simple methods by which mixtures of the latter substances were separated.

The study of chemistry is vitally concerned with chemical compounds, but it is concerned to a much smaller extent with mixtures. For in mixtures there is no real association of the component substances and a study of the properties of the mixture is only a study of the properties of the separate substances. But in compounds, on the other

hand, the characteristics of the constituent substances are lost and the compounds themselves are distinctive chemical individuals with distinctive properties of their own.

SUMMARY

An element is a substance which cannot be resolved into different chemical substances by any agency under human control. All the matter of which our earth is composed is made up of about eighty elements.

Chemical compounds are pure substances which can be separated by chemical means into two or more elementary substances. Chemical compounds are characterized by a definite ratio by weight of their constituent elements.

Questions

1. Define element ; compound.
2. Name five common elements.
3. Name five common compounds.
4. In the light of our present knowledge of the elements, can we ever hope to be able to convert lead into gold?
5. What is true of the proportions of the constituents of a compound that is not true of the components of a mixture?

CHAPTER IV

COMBUSTION

THE chemical phenomenon most familiar in everyday life, in fact so familiar that the average person hardly realizes that it has any connection with chemistry, is ordinary burning or combustion. Combustion is, however, not only the most common, but also one of the most important, of chemical reactions, since it is the energy liberated in this reaction which furnishes the human race with most of its heat, light, and power.

15. Historic Views as to the Nature of Combustion. Common as is the phenomenon of fire, it is, until understood, most mysterious. Fire was regarded by the ancients as one of the gifts of the gods. By the Greek philosophers it was regarded as one of the four elements of which the world is composed. At a later period it was regarded as consisting in the escape of a volatile substance called phlogiston, which was supposed to be contained in all substances capable of burning. It was only during the last of the eighteenth century and in the beginning of the nineteenth that the true chemical nature of combustion gradually came to be appreciated. This was scarcely more than a century ago, and since combustion is one of the most important of chemical phenomena and since an explanation of its nature first led to an understanding of other chemical phenomena, it is plain that chemistry is still a comparatively young science.

16. Modern Theory of Combustion. Combustion consists of a chemical uniting of the combustible substance with oxygen, a substance which is one of the components of the air; the product of this union is in many cases a gaseous substance, but in all cases, whether the combustion product be a solid, a liquid, or a gas, its weight is exactly equal to the weight of the substance burned plus the weight of the oxygen consumed.

17. Growth of Modern Theory of Combustion. Let us outline a few of the important facts regarding combustion and recount some of the important steps by which the modern view of the nature of combustion was developed.

Wood, coal, and charcoal, if kindled, that is if heated sufficiently so that active combustion begins, will burn, and what we call fire is observed. Flames which are hot and luminous arise and then seem to vanish into the air.

Combustion is not limited, however, to those cases where substances burn vigorously with a flame. Even the earlier chemists who upheld the phlogiston theory realized that the burning of wood and the rusting of iron were phenomena of a similar nature. Their mistake lay in thinking that in each case there was an escape of phlogiston. When iron rusted, they thought that phlogiston escaped, and that the rust left, or the *calx*, as it was then termed, was iron which had lost the phlogiston which belonged to it. We now know that iron rust is produced by the slow combining of iron with oxygen, and that the weight of the rust, or oxide, is exactly equal to the sum of the weights of the iron and the oxygen consumed.

Much iron oxide is found in the earth as a brown or black ore, and to obtain the metal this ore is heated in a furnace with charcoal or coke which removes the oxygen from the

oxide and leaves uncombined iron. This process for obtaining iron from its ore is a very ancient one, and was well known to the phlogistic chemists, but they imagined that charcoal was pure phlogiston and that it combined with the calx (iron oxide) to produce the metal, which they regarded as the compound of the calx and phlogiston. They failed to appreciate and correctly interpret the fact that the calx weighed more than the metal.

18. Use of the Balance. When, however, the balance came into general use as a necessary instrument in the study of chemistry and the fact that metal oxides weigh more than the metals from which they are formed became better understood, the old phlogistic idea of combustion gave way in favor of the modern theory of oxidation.

19. Oxidation of Metals. Iron is not the only metal which on exposure to the atmosphere becomes coated with a dull non-metallic layer. In fact, most of the better-known metals, with the exception of the precious metals, gold, silver, and platinum, are soon tarnished or corroded to a greater or less degree, depending on their chemical activity and on whether the coating first formed is permeable or impermeable to the gases of the air.

Lead, copper, and zinc, for example, when freshly polished, display bright metallic surfaces; but after exposure to the air, as when they are used for gutters or for trimmings on roofs, lead becomes covered with a gray and lusterless coating, copper with a green coating, and zinc with a dull whitish coating. If instead of being exposed to the weather these metals are heated in contact with the air, a more rapid change occurs. Lead, if it is kept above its melting temperature and stirred so as to have a fresh surface continually exposed, changes in a fairly short time to a dull yellow

powder. Copper when heated to redness becomes covered with a black or reddish crust which can be scraped off as a brittle scale. Zinc if heated to a high temperature catches fire and burns with an intense bluish white light and a fine white powdery substance (zinc white) is formed. In all these cases it was found, when the balance was used, that the product of the combustion was heavier than the original

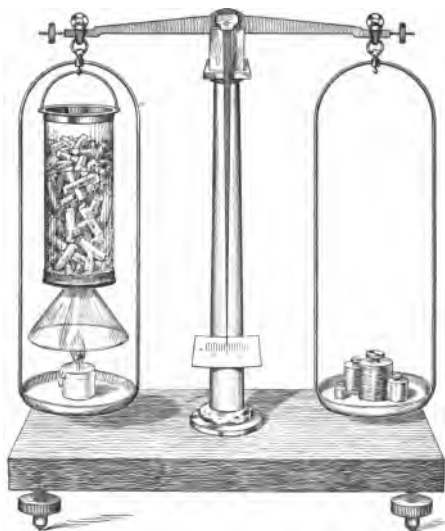


FIG. 2. — For showing that the Products of Combustion of a Candle weigh more than the Candle Itself. The candle is placed on one pan of the balance and above it is suspended a glass cylinder filled with sticks of sodium hydroxide. Weights are then placed on the other pan to exactly counter-balance the candle and absorption cylinder. The candle is now lighted, the gases from the flame pass through the funnel into the absorption tube; the pan with the candle soon sinks, showing that it is growing heavier. To keep it in balance more weights must continually be added to the other pan as long as the candle burns.

metal; furthermore it was observed that when a metal had once been heated or charcoal burned in a quantity of air confined in a closed vessel, the residual air had no further power to cause corrosion or burning. It thus became apparent that in combustion some component must be taken from the air to combine with the combustible substance.

20. The Products of Combustion of a Candle. It can be shown by the balance that there is an increase in weight, not only when metals

corrode to form solid oxides, but also in those cases in which substances burn to form gaseous products. Thus, for example, a balance may be arranged with a candle on one pan and suspended above it a lamp chimney containing sticks of sodium hydroxide to absorb the products of combustion (Fig. 2), and the whole may be exactly counterpoised by placing weights on the other pan. So long as the candle remains unlighted, the pans remain balanced and neither rises or falls. When the candle is lighted and begins to waste away, one would expect the pan holding it to rise because of a decrease in weight. What is actually seen is that that pan sinks. The gaseous combustion products of the candle have been caught by the sodium hydroxide and these are thus shown to weigh more than the candle alone.

21. Discovery of Oxygen by Priestley, 1774. The discovery of pure oxygen by Priestley paved the way for recognizing the true nature of combustion, although Priestley himself was unable to fit together the facts and deduce the true solution.

Mercury, on account of its remarkable properties, was always a favorite substance for experimentation with the early chemists. It had been known that if this metal was maintained at a temperature just below its boiling point (considerably below a red heat) it slowly changed into a bright red powder — the calx of the phlogistic chemists. Priestley put some of the red powder in the top of a glass tube filled with mercury and placed it with its closed end up and its lower end sealed by being dipped in a vessel of mercury. By focusing the sun's rays by means of a burning glass upon the red powder at the top of the tube, he found that a gas was formed which forced down the mercury and

filled some little space. On placing a lighted candle in this gas, he found that it burned with a remarkably brilliant flame — far more brilliant than when it burned in ordinary air. He was much mystified by this behavior, and he described the gas as having all the properties of ordinary air only in much greater perfection. He called it dephlogisticated air and regarded it only as very pure ordinary air.

22. Lavoisier's Explanation of Combustion. It remained for the French chemist Lavoisier to clearly recognize and state the true nature of combustion. He connected Priestley's discovery with the fact that an increase rather than a decrease in weight takes place when substances burn, and with the fact that during the burning the air not only loses in volume, but also loses its power to support combustion.

Lavoisier's crucial experiment was to heat mercury within an inclosed vessel of air. He found that the volume of the air contracted by about one fifth, while at the same time a red powder formed on the surface of the mercury; the residual air had no power to support combustion. Afterwards, on heating this red compound of mercury, a gas was given off whose volume was one fifth that of the original air. This gas alone supported combustion with great vigor, and when mixed with the residual four fifths of the original air, restored to it the property of supporting combustion in the ordinary manner.

23. Combustion in the Light of our Present Knowledge. The atmosphere consists chiefly of a mixture of two gases, — about one fifth part by volume is oxygen, the supporter of combustion; about four fifths is nitrogen, an inert gas which plays no part in combustion except that it dilutes the oxygen and decreases the intensity of its action.

When substances burn in the air, they combine chemically

with the oxygen to form *oxides*, while the nitrogen is left unchanged. An oxide is a chemical compound of an element with oxygen and nearly all of the elements are capable of forming oxides.

24. Oxides of Carbon. Charcoal, which is nearly pure carbon, burns vigorously when it has a plentiful supply of air and forms carbon dioxide, an invisible gas. If all or nearly all of the oxygen of the air is used up in this way, the latter can no longer support combustion; neither is air that is so deprived of its oxygen able to support human or animal life. Carbon dioxide is not actively poisonous, but the absence of oxygen results in suffocation.

If the charcoal is burned with a restricted supply of air, then a part or even the whole of the product of combustion consists of carbon monoxide, another oxide of carbon which contains a lesser proportion of oxygen. This substance is also a gas, but it is extremely poisonous when breathed by human beings or animals. It is due to the formation of this gas that charcoal fires in unventilated rooms have been responsible for many deaths.

25. Combustion of Wood. Wood is a compound containing carbon, hydrogen, and oxygen. When it burns the chemical reaction is not unlike that of burning charcoal. The existing form of chemical combination of the wood is broken down by the heat of the fire, and the carbon and hydrogen combine with oxygen from the air in addition to that which comes from the wood itself and form carbon dioxide, and oxide of hydrogen (water vapor), respectively.

When wood decays, it undergoes a chemical change not essentially different from that of burning except in rapidity. The heat of the reaction is not produced fast enough to cause flame or even to make the wood feel warm to the

touch, but still the products of the reaction contain carbon dioxide and water.

26. Slow Combustion of Foods in our Bodies. The source of the body warmth and muscular energy of men and animals lies in a chemical reaction similar to that of the burning or the decay of wood. The burning of wood is a violent reaction and produces intense local heat; the combustion of foodstuffs in animals, on the other hand, takes place slowly, like the decay of wood, and produces only the degree of warmth necessary to keep the animal in health. A furnace fire is fed with coal or wood. The fire in a man's body is fed with the foods that contain sugar, starch, or fat. Sugar, starch, and fat have a chemical composition somewhat similar to that of wood; that is, they are composed of carbon, hydrogen, and oxygen. In the digestive organs they are made soluble and pass into the blood and are taken by the blood into all the tissues of the body. In the tissues, to which the blood also brings oxygen, taken from the air that is breathed into the lungs, there takes place the most marvelously regulated combustion. This combustion, like the active burning of wood in the air, results in the formation of carbon dioxide and water, and both of these products are exhaled with every breath from the lungs. To demonstrate that water vapor is present in the air from the lungs, one has only to breathe against a cold window pane, when the glass becomes clouded with condensed droplets of water; and to show the presence of carbon dioxide, one need only blow the breath through a glass tube into a tumbler of lime-water, which is immediately rendered white and cloudy.

When we exercise violently, our breath comes much faster. This is because the waste or combustion of bodily tissue is much more rapid during exercise and more oxygen

has to be supplied from the lungs to consume it. Also it is necessary for the lungs to work more rapidly in order to remove the greater amount of carbon dioxide which is produced.

27. Forced Draft. A similar case of the need of an increased supply of oxygen when more rapid combustion is desired, is seen in the use of the blacksmith's bellows. In order to hasten his fire, the blacksmith pumps air rapidly through the fire by means of the bellows, thus supplying more oxygen and hence burning more fuel in a given time and producing a hotter fire.

A battleship uses a forced draft, that is, it pumps air rapidly through the fires, when attempting to attain a high speed. The principle is, of course, the same as that involved in the blacksmith's fire; a limited amount of air can burn only a limited amount of coal and thereby produce only a limited amount of heat. By supplying more air, more coal can be burned and more heat obtained.

28. Smoke and Smoke Prevention. It is not an easy matter to regulate the proper supply of fuel and air in the fires of manufacturing establishments, or, for that matter, in other fires, and as a consequence our manufacturing cities are to-day burdened with the smoke nuisance. The obnoxious black smoke which issues from the chimneys consists in the main of unburned fuel material, for the most part in the solid condition, but so finely divided that it floats for a long time in the air just as fine dust will do.

There is, however, no good excuse, now, for allowing the smoke nuisance to continue. Modern smoke-preventing devices are designed in the first place to regulate the supply of both the air and the fuel so that neither an excess of fuel shall be wasted as smoke nor too great an excess of air shall

enter, to cool off the fire and diminish its efficiency. This regulation is usually accomplished by means of some form of automatic stoker which can be made to supply the fuel as rapidly or as slowly as desired, while the air supply is controlled by a blower. In the second place, it is necessary that the smoke which does form shall be burned before it can pass into the cooler flues and become chilled to a temperature below its burning point. This is accomplished by admitting some fresh air into the chamber above the fire and allowing this, mixed with the hot gases and smoke, to pass through a considerable distance over the white-hot fire bed between it and the arch of very hot fire brick which forms the top of the furnace. In this way the smoke, together with sufficient air, is kept at a temperature above

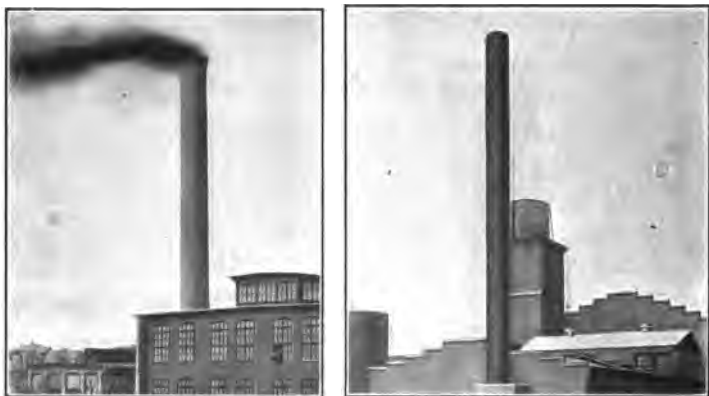


FIG. 3. — **Smoke Nuisance and Smoke Prevention.** Automatic stoker and large combustion chamber used in furnace whose chimney shows no smoke.

its kindling point until it is completely burned. Such smoke consumers are now largely used, and allow the burning of even the cheapest grades of soft coal in the powdered form

without an objectionable amount of smoke issuing from the chimney. The saving due to the economy of fuel, in many cases, more than offsets the cost of the smoke prevention devices.

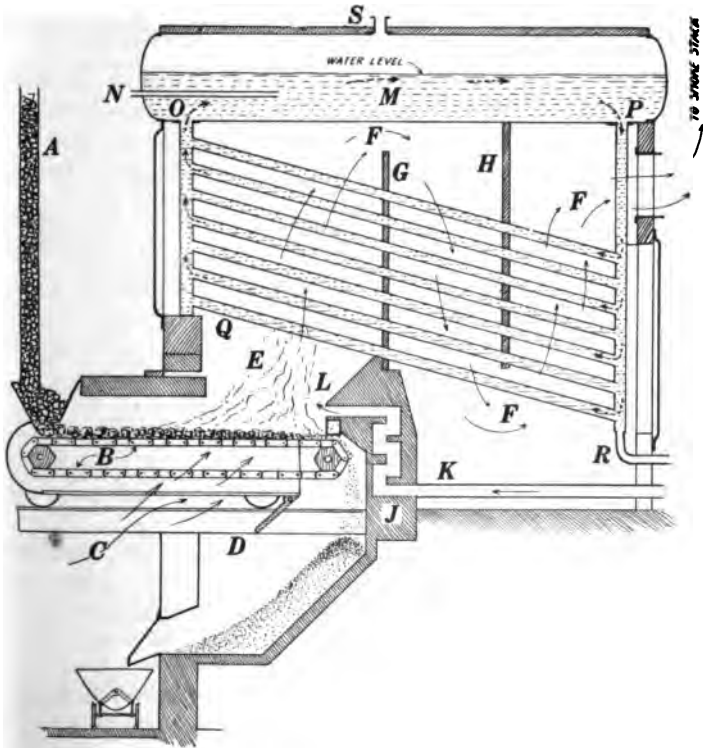


FIG. 4. — Boiler and Furnace with Chain Grate Stoker.

- | | |
|--------------------------------|---------------------------------|
| A. Coal chute. | wall for delivering heated |
| B. Chain grate. | air to fire. |
| C. Air inlet. | M. Water in drum. |
| D. Damper. | N. Water inlet. |
| E. Flames. | O-P. Outlet and inlet for water |
| F. Course of heated gases. | circulation. |
| G-H. Baffle walls. | Q. Water tubes. |
| J. Bridge wall. | R. Blow-off pipe. |
| K-L. Zig-zag passage in bridge | S. Steam outlet. |

SUMMARY

The discovery of oxygen by Priestley in 1774 was the first step towards understanding the nature of combustion. Somewhat later Lavoisier developed the present explanation by connecting Priestley's discovery with the fact, shown with the chemical balance, that an increase in weight always occurs during combustion.

Combustion is the most frequently observed as well as the most important of chemical changes. Combustion consists in the uniting of oxygen, the active component of the air, with the combustible substance. In rapid combustion great heat is developed and incandescence, or flame, is observed.

Slow combustion, as the rusting of iron, or the decay of wood, is chemically the same sort of a process as rapid combustion, but the heat produced has time to escape so that no incandescence, or flame, is to be seen. Food is the fuel for the bodies of men and animals, and by a process of slow combustion it furnishes animal warmth and muscular energy.

Oxides. Most metals give solid oxides as combustion products. Carbon gives two different oxides: with a plentiful supply of air, carbon dioxide, a comparatively harmless gas; with a restricted supply of air, carbon monoxide, a most poisonous gas.

Fuels contain carbon as their most important constituent, and besides carbon they usually contain hydrogen. Their material combustion products are principally gases and are of no value. They are burned for heat, light, and power, which are essential for the welfare of the human race.

Smoke consumption. As ordinarily burned, much fuel is wasted as smoke, but by the use of suitable devices this waste may be prevented and the nuisance of smoke avoided.

Questions

1. How might one prove that something from the air is concerned in combustion?

2. Why does the rusting of iron continue until all the iron is rusted, whereas the tarnishing of copper, zinc, and lead is on the surface only?

3. Why, then, is it necessary to paint iron bridges, although it is not necessary to paint copper-covered roofs?

4. Explain the danger from charcoal fires in closed rooms. Why is there not the same danger from a burning gas jet?

5. Give some evidence to prove that combustion takes place in the animal body.

6. Discuss from a common viewpoint the rapid breathing of a person running and the use of a blacksmith's bellows.

7. What is smoke? Why is it an economy to prevent it?

8. When burning dry leaves, if one rakes a lot of new leaves all at once on top of the fire a very dense smoke is formed. Explain why it is that when the flame finally works up through the new leaves and bursts out through the top, the smoke all seems to vanish.

9. Explain why in unprogressive manufacturing establishments black smoke belches from the chimney when the stoker opens the furnace door and shovels a quantity of soft coal on the fire. How might the stoker by care lessen the amount of smoke? How would you design and run a furnace to prevent smoke?

10. What does the fact that a pile of barnyard manure steams in winter indicate is taking place within the pile?

11. Why does a camper get down and blow his fire when it gets low?

12. Why does water extinguish a fire?

CHAPTER V

OXYGEN

IN the last chapter it has been seen that the atmosphere contains a chemically active substance which is called oxygen; and that when any one of a number of metals is heated in the air, this oxygen combines with the metal to form an oxide. It was by heating one of these oxides, namely oxide of mercury, that pure oxygen was discovered by Priestley.

29. Abundance. Oxygen is now known to be the most abundant of all the elements, for it is estimated that about one half of the whole earth, as far as we know it, is composed of oxygen. Uncombined oxygen comprises about one fifth of the air. Eight ninths by weight of water is oxygen, which is in combination with hydrogen. The great bulk of the solid crust of the earth is composed of compounds of oxygen; thus quartz rock and ordinary sand, which is quartz in a fine state of subdivision, are oxide of silicon, containing 53 per cent of oxygen; limestone consists of two oxides in combination, calcium oxide and carbon dioxide, 48 per cent by weight of the limestone being oxygen.

30. Preparation by heating Oxides. The method of Priestley for the preparation of oxygen is still used as a convenient laboratory method for showing that oxygen can be generated from an oxide; it is never used, however, to prepare any large quantity of oxygen, because mercury and its compounds are too costly.

Many less expensive oxides will evolve oxygen when heated sufficiently, but in most cases the amount of heat required is so great that the process is too costly or too inconvenient on that account.

31. Preparation from Potassium Chlorate. For the preparation of oxygen on the small scale in the laboratory, recourse is had to potassium chlorate, which contains about 40 per cent by weight of oxygen and gives it all off when heated. The potassium chlorate is mixed with its own bulk of powdered manganese dioxide, and the mixture is placed in a test tube (Fig. 5).

The latter is provided with a delivery tube leading to a water trough, and on gently heating the test tube oxygen gas is evolved and can be collected in test tubes or in wide-mouthed gas bottles which have

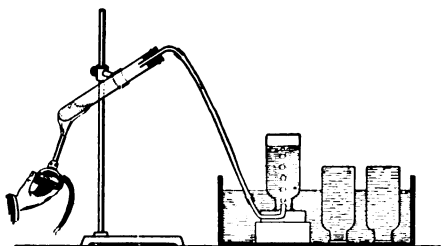


FIG. 5.—Preparation of Oxygen. Potassium chlorate mixed with manganese dioxide is heated and the gas is collected over water.

been previously filled with water and inverted in the trough.

The manganese dioxide and the potassium chlorate both contain oxygen, and either alone will give up oxygen upon being strongly heated. The potassium chlorate, however, requires to be heated to considerably above its melting point (334°C.) before giving up its oxygen rapidly, and the manganese dioxide when alone yields oxygen only when heated to a red heat. If, however, the two substances are mixed together and heated, oxygen begins to come off at a temperature in the neighborhood of 200°C. Hence the mixture is invariably used.

32. Catalysis. If the separate substances are carefully weighed before they are heated and the products left after the decomposition are separated and also weighed, it is found that exactly as much manganese dioxide remains as was taken at the start, while in place of the potassium chlorate, a new substance, potassium chloride, is left. The latter contains no oxygen, and it is clear therefore that all of the oxygen has come from the decomposition of the potassium chlorate. The manganese dioxide has suffered no apparent change, but has, by its mere presence, helped the other substance to undergo a change very much more smoothly and quickly than it could have done alone. Cases like this we shall find are very frequent in chemistry and they are known as cases of *catalysis*. The catalytic agent (in this case the manganese dioxide) does not cause the reaction, it merely makes it easier for it to take place. No more does lubricating oil cause a wheel with a rusted bearing to turn, it simply makes it easier for it to turn.

33. Preparation from Liquid Air. The most inexpensive source of oxygen is obviously the air, and comparatively recently a method of cheaply separating it from the air has been perfected. By the Linde process, the air is first liquefied by high compression and intense cold, and the liquefied air within the apparatus is then allowed to boil, whereby nitrogen, which is the more volatile component of the air, passes off, leaving fairly pure oxygen. The latter is then allowed to vaporize and is pumped under high pressure into steel cylinders, in which it is transported and sold.

34. Properties of Oxygen. When oxygen prepared by one of the above methods is examined, it is found to be a colorless, odorless, tasteless gas and one which will cause a glowing splinter to burst into a vigorous flame, but will not

itself burn. These properties can be discovered without the use of any elaborate apparatus and without any great degree of skill in observation. If we were to obtain a gas

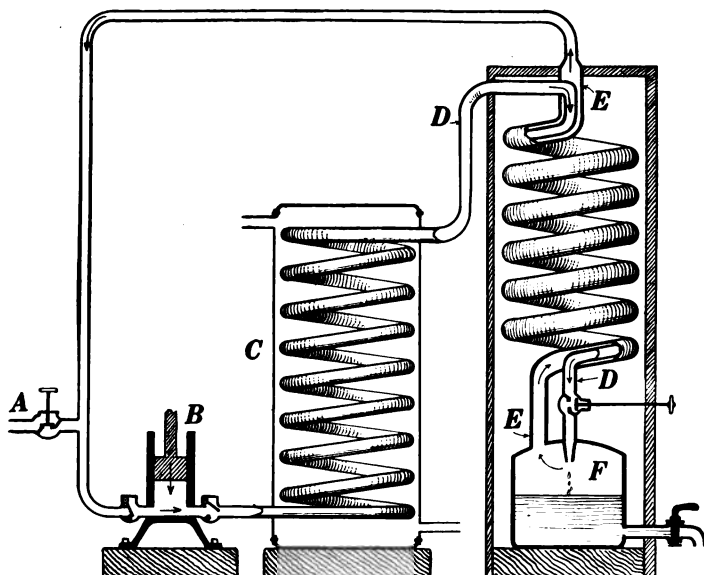


FIG. 6. — Linde Apparatus for making Liquid Air. *A*, air inlet. *B*, compressing pump. *C*, cooling coil where the heat developed by the compression of the air is withdrawn. Coil is surrounded by running cold water. *D*, inner pipe of the liquefying coil; here the compressed air is cooled to a very low temperature. *E*, outer pipe of liquefying coil; here the expanding air cools the compressed air in *DD*. *F*, expansion chamber and reservoir for liquid air. The air emerging from the valve at lower end of *D* expands suddenly and produces great cold. Part of the air is thus liquefied and drops into the reservoir while the rest passes through *E* and cools the compressed air in *D* to the liquefaction point.

from some unknown source and find that it possessed the properties mentioned, it would be natural to assume that it was oxygen. There is at least one other gas, however, — and there might be more, — which shows approximately the

properties mentioned, and it might be possible for us to obtain this gas and mistake it for oxygen. Hence in order to distinguish oxygen with certainty from all other substances, we must define its properties more completely and more exactly.

Properties such as the specific gravity, the degree of solubility in water, and the temperature of liquefaction and of solidification can be accurately measured and stated in exact numerical terms. It is extremely improbable — we can even say impossible — that a substance can have all the easily observed properties of oxygen, noted earlier, and give exactly the same quantitative values for the last-named properties, and still be any other substance than oxygen. Of course, if the substance were further studied and found to differ from oxygen in any single particular, it could not be oxygen; but it is our experience with nature that when two substances are exactly alike in several of their properties they will be found to be alike in all of their properties.

35. Density. Oxygen is a little heavier than air, its specific gravity referred to air being 1.105, that is, one liter of oxygen weighs 1.105 times as much as one liter of air at the same temperature and under the same pressure. Expressed in other terms, one liter of oxygen at 0° C. and under 760 millimeters pressure (that is under *standard conditions*) weighs 1.43 grams; that is, 1000 cubic centimeters of oxygen weigh about the same as one and one half cubic centimeters of water.

36. Solubility. Oxygen is slightly soluble in water. At ordinary temperature and pressure about three volumes of oxygen dissolve in one hundred volumes of water. Thus oxygen is available to fishes, for it can pass from solution in water into the blood of the fishes through the delicate mem-

branes of the gills, — the gills serving fishes in the way that the lungs serve human beings.

As is the case with all other gases, oxygen is more soluble in cold water than in warm water. It is a frequently observed fact that when a glass of freshly drawn cold water is allowed to stand in a warm room little bubbles form and cling to the side of the glass. These bubbles are composed in part of oxygen. Besides being essential to the life of fishes, the oxygen dissolved in water plays a large part in purifying natural waters from sewage and other contamination. Many of the harmful substances contained in sewage combine with oxygen and are thus converted into harmless compounds.

37. Liquid and Solid Oxygen. We are familiar with oxygen only as a gas, but to the scientist with the requisite apparatus, liquid and solid oxygen are familiar forms, just as ice is to the everyday man a familiar form of water. If oxygen gas is kept in a vessel at the ordinary pressure and cooled sufficiently, it will condense to a liquid when the temperature of -182.5°C. is reached. This same temperature, -182.5°C. , is also the *boiling point*, because if liquid oxygen is allowed to stand in an open vessel it boils at this temperature, that is, bubbles of gas form within the body of the liquid, rise to the surface, and escape. In the same way water boils at 100°C.

The liquid oxygen has a blue color, it is somewhat heavier than water, its specific gravity being 1.13, and it shows the surprising property of being magnetic.

On cooling liquid oxygen still further, it changes to a solid at about -200°C. in the same way that water changes to ice at 0°C.

38. Chemical Properties. The most marked chemical property of oxygen is its great combining activity. Com-

pounds of it with every other element, except fluorine and certain inert gases of the atmosphere, are known. Moreover, it will combine with most of the elements directly, particularly when heated with them. This was seen in Chapter IV to be the case with many metallic elements, and it is likewise true of many non-metallic elements such as phosphorus, sulphur, and carbon.

39. Oxides. The product formed by the union of oxygen with another element is called an *oxide*. It is a custom among chemists in naming compounds consisting of only two elements to use the name of the more metallic element in full and the root of the name of the more non-metallic element together with the termination *ide*. Thus sulphur and oxygen form sulphur oxide; iron and oxygen form iron oxide.

40. Combustion in Pure Oxygen. Fuels when once kindled react vigorously with the oxygen of the air giving heat and light; many metals when wet rust or corrode slowly, which is in the main a combining with oxygen. The power to support active combustion is much stronger with pure oxygen than with air. For example, a lump of charcoal with a barely glowing spark flames up brilliantly when thrust into a jar of pure oxygen. Burning bits of sulphur or phosphorus burn far more vigorously in pure oxygen. Even a piece of iron wire, if a glowing bit of wood is attached to its end, will burn vigorously and throw off a beautiful shower of sparks, when lowered into pure oxygen.

41. Kindling Point. At ordinary temperatures, most combustible materials do not burn,—not even in pure oxygen. If they are dry, most materials can be preserved almost indefinitely in oxygen without a perceptible amount of chemical union. Thus dry, cold oxygen is pretty nearly

an inert substance chemically. It is probably not absolutely inert, however, for there is perhaps a slow combustion always taking place, even although not enough change may occur in one hundred or one thousand years to be noticeable.

Now it is a general rule that chemical reactions take place faster the higher the temperature. Let us apply this rule, for example, to a piece of dry wood which at ordinary temperature does not combine perceptibly with the oxygen of the air; if the wood is placed in a cooking oven, it combines without doubt far more rapidly, but the reaction is still too slow to produce more heat on its own account than can easily escape. Placed in hotter and hotter places, the wood reacts more and more rapidly, until at length a point is reached at which the heat is produced more rapidly by the reaction than it can escape from the vicinity of the wood. At this point the wood bursts into flame, for since the heat cannot all escape it must raise the temperature about the wood still higher and this higher temperature must produce a more rapid reaction which must in turn raise the temperature still higher.

The kindling temperature is that temperature at which a slow combustion changes abruptly to a rapid one and a corresponding sudden rise in temperature occurs.

The kindling temperature of different substances is very different. Thus yellow phosphorus catches fire when exposed to air even at the ordinary room temperature, sulphur has to be heated moderately, whereas charcoal must be raised to a red heat before it will burn.

42. We can now appreciate why an iron wire burns brilliantly in pure oxygen, but not at all in air. The kindling temperature of iron is high. When once it is reached in pure

oxygen, the heat of the chemical action is enough to maintain the temperature above this point. But in air there are four volumes of inert nitrogen to each volume of oxygen, and the nitrogen as well as the oxygen has to be raised to the kindling temperature of the iron if the iron is to continue to burn. In addition to this the oxygen is impeded by the nitrogen in reaching the surface of the iron.

In extinguishing a fire with water, the main function of the water is to cool the burning objects to below the kindling temperature.

43. Spontaneous Combustion. In some cases of slow oxidation the amount of heat given off, although not enough to cause the kindling of the substance concerned when it is freely exposed to the air, is yet sufficient to set fire to it, if in a situation from which it is difficult for heat to escape. Oily rags sometimes cause fires in this way, if thrown into corners. Some kinds of oil oxidize quite perceptibly even at ordinary temperatures. When the rags are packed together so that the heat produced by this slow combustion cannot escape, the temperature rises until the mass breaks into flame. This type of action is called spontaneous combustion, and it is a very frequent cause of factory fires.

44. Slow Combustion. Dry oxygen is almost inert at ordinary temperatures, but dissolved in water it is capable of reacting slowly, as is shown by the rusting of moist iron. In the human body the oxygen dissolved in the blood combines with the elements of the food, giving the warmth and energy necessary to the human being. This is a wonderfully regulated slow combustion, for in normal health it is never allowed to carry the temperature much above the normal body temperature of 37° C. nor to let it get much below that mark in cold weather.

45. Decay of Wood. Dissolved oxygen is also responsible for the decaying of wood, which is also a case of slow combustion. We often see perfectly sound timbers in houses over a century old where the rain has been carefully kept out, but the same timbers thrown out on the moist ground are rotted through in a year or two. Moisture, however, is not all that aids in the decay of the wood; an important part is played by bacteria, microscopic living organisms, which in the chemistry of their life processes bring about the oxidation of the wood in much the same way as animals bring about the oxidation of their food. Wood that is to be used in wet places, as for example, piles for buildings, is preserved by being saturated with creosote or other material poisonous to bacteria.

Dry wood does not decay because the bacteria can live only when wet or at least moist. Painting preserves wood because it excludes both moisture and oxygen.

46. The spoiling of food is similar to the decay of wood in that it is due to chemical changes which are promoted by bacteria, although many of these changes consist only of the partial decomposition of the complex compounds of which food consists, and do not involve any action of the oxygen of the air. Thus the souring of milk is due to a decomposition of milk sugar into lactic acid under the influence of a certain kind of bacteria. The fruit sugar of apples decomposes into carbon dioxide and alcohol under the influence of yeast cells when sweet cider ferments. When cider or wine turn to vinegar it is due to the oxidation of alcohol to acetic acid through the agency of the acetic bacteria. This change is an oxidation and it can only progress when the cider or wine is exposed to the air. The well known "mother of vinegar" which is often seen in vinegar bottles consists of a

cohering mass of the acetic bacteria. When meats and fish spoil the products are very poisonous and this kind of spoiling may take place in the absence of oxygen.

Anything which will kill bacterial life will stop the spoiling of food. Thus to make milk keep longer without souring, we heat it. In canning fruit or meat, the material is heated as high as the boiling temperature of water in order to kill bacteria. In the packing houses, the cans after sealing are invariably heated again to assure the destruction of all bacterial life.

SUMMARY

Oxygen is prepared in bulk, most cheaply by methods by which it is extracted from the air, but for the laboratory the most convenient method is to heat potassium chlorate, to which some manganese dioxide has been added.

Properties of Oxygen. Oxygen can generally be recognized by its easily observed properties. It is a colorless, odorless gas, slightly soluble in water. The most marked chemical characteristic of oxygen is its great power to combine with other elements. Oxygen under standard conditions weighs 1.43 grams per liter.

The kindling temperature is the lowest temperature at which slow combustion changes to rapid combustion. The kindling point is different for different substances. Above the kindling temperature, oxygen combines violently with many substances.

Slow combustion consists in the union of a substance with oxygen, below its kindling temperature, as in the rusting of iron, the decaying of wood, and the spoiling of food. The latter two actions are promoted by bacterial life.

Spontaneous combustion results when, during slow combustion, heat accumulates until the kindling temperature is reached, then the substance takes fire.

Questions

1. What is the most prominent chemical property of oxygen?
2. Why do metals, such as copper, lead, and zinc, which oxidize

quickly when hot, wear as well as they do when exposed to the air on roofs?

3. Why does not gold corrode?

4. What would be the effect of using pure oxygen in the blacksmith's bellows?

5. Give reasons why it is fortunate that the atmosphere does not consist entirely of oxygen.

6. In view of the combustibility of wood, why is it that the fire danger in wooden buildings is so slight?

7. Under what conditions do fires sometimes start without the application of a flame?

8. Would oxygen be a useful gas with which to fill balloons? Explain.

9. How do fish breathe? What would be the effect of putting goldfish in distilled water? Why would freshly distilled water lack oxygen?

10. Explain why a fallen tree in the forest disappears after a period of years.

11. It is unsafe to drink water from a river that has been freshly contaminated with sewage. How is oxygen responsible for making the water safe to drink after it has run for miles over rapids in a river?

12. How does (a) canning, (b) smoking, (c) salting, (d) refrigerating, (e) drying, and (f) preserving in sirup, prevent in food products the kind of slow oxidation called decay?

CHAPTER VI

THE OXIDES OF CARBON

IN the preceding chapters it has been seen that when the element carbon burns, it unites with oxygen of the air to form a gaseous product which is always carbon dioxide when sufficient air can come in contact with the burning object, although carbon monoxide may result with insufficient air.

47. Enormous Production of Carbon Dioxide. Enormous quantities of charcoal, coke, coal, and wood, — fuels which consist largely or wholly of carbon, are being burned all the time. Added to this artificial combustion, we have an even greater production of carbon dioxide by the slow combustion of food in human beings and animals and of wood and dead leaves in the process of decay. It has, in fact, been estimated that 97 per cent of the carbon dioxide turned into the air is the product of decay.

48. Utilization of Carbon Dioxide by Plants. In view of the great amount of carbon dioxide produced, it would seem as if the air must become filled with this gas. Still it is a fact that pure air in the country never contains more than three or four one hundredths of 1 per cent of it. How can it be that such large quantities of this gas are all the time being put into the air and yet the amount present never increases? It must be because carbon dioxide is being continually withdrawn from the air. The study of the life of green plants has shown that it is they that perform this

service; they require carbon dioxide for their development, and their green leaves take in the carbon dioxide from the air. But this is not all. The lungs of animals withdraw oxygen from the air and give back carbon dioxide; the green leaves of plants withdraw the carbon dioxide and after appropriating the carbon in their chemical life processes, give back the oxygen. Thus there is a continuous interchange between animals and plants, each utilizing what is a waste product from the other, and with these two agencies at work the quantity of carbon dioxide in the air never varies much from the mean of 0.04 per cent.

49. Source of Pure Carbon Dioxide. In our laboratory study of carbon dioxide our first task is to collect some of this gas pure. One might first think to do this by collecting the gaseous combustion products of charcoal, but it would prove difficult to get the gas in this way unmixed with nitrogen and unconsumed air. Our best source of carbon dioxide has been found to be limestone, a rock that is very abundant in the earth.

50. Limestone. In past geologic ages, plants have been absorbing carbon dioxide from the air, just as at present. Certain low orders of sea animals also have been utilizing carbon dioxide in the formation of their shells, in which it becomes combined and held in the form of calcium carbonate. Coral, for example, and the shells of oysters and clams consist largely of calcium carbonate. Masses of these and similar shells which accumulated in past ages, have been deeply covered by deposits of earth. They have since been transformed gradually, through the agency of great pressure and heat, into compact masses of limestone.

A very pure variety of limestone is marble, and in the laboratory we shall use marble as the source of carbon dioxide.

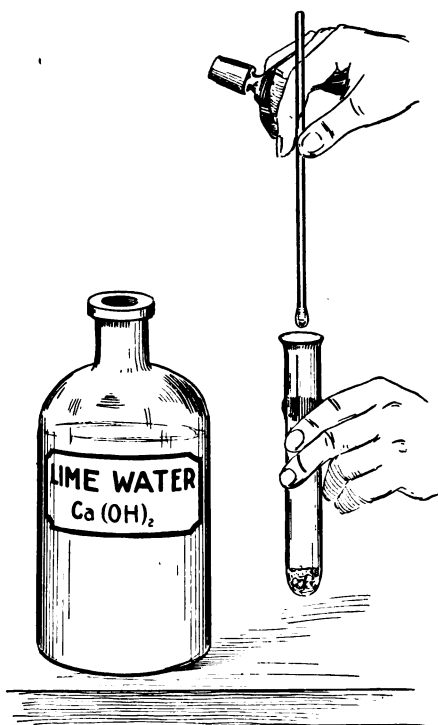


FIG. 7. — Test for Carbon Dioxide. A clear drop of limewater suspended on a stirring rod is rendered milky if lowered into a vessel containing carbon dioxide. Notice that the stopper of the limewater bottle is held between the third and fourth fingers at the back of the right hand instead of being laid on the desk top where it may be contaminated before being replaced in bottle.

It is only necessary to treat this substance with a dilute acid when carbon dioxide is liberated, while the product formed from the calcium and the acid remains behind.

51. Means of recognizing Carbon Dioxide. If a pinch of powdered marble is placed in a test tube and covered with a few cubic centimeters of dilute acid, — hydrochloric acid, for example, — a vigorous effervescence¹ takes place and continues until either the marble or the acid is all used up.

If a lighted taper is inserted into the

test tube while the effervescence is taking place, the flame is

¹ Effervescence consists in the rapid evolution of bubbles of a gas and in this respect it has somewhat the appearance of boiling. It is, however, an entirely different phenomenon from boiling, since in boiling the vapor that rises is always the same substance as the liquid from which it comes.

extinguished. This accords with our knowledge that carbon dioxide is a non-supporter of combustion. If a stirring rod is dipped into a bottle of clear limewater and then withdrawn so that a clear drop hangs from its lower end, and if this is then lowered into the test tube, it immediately becomes clouded or milky in appearance. This test has already been mentioned and is one of the most distinctive tests for carbon dioxide.

If the last two tests are made repeatedly in inverted and upright test tubes in which carbon dioxide has been generated, it will be found that all evidence of the gas disappears in a moment from an inverted test tube, whereas it persists for some time in an upright test tube. This shows that carbon dioxide must be heavier than air.

The three properties of carbon dioxide enumerated in the last few paragraphs, namely its power to extinguish flame, its ability to render limewater milky, and its being heavier than air, are all properties which can be recognized with great ease and it is these properties for which we first look when we wish to find out whether a given gas is or is not carbon dioxide. If we find the gas to possess these three properties, we are reasonably certain that it is carbon dioxide.

Of course to render identification of this gas absolutely certain, its properties must be observed with much greater exactness and to accomplish this it is necessary to prepare some considerable quantity of the gas and to collect it unmixed with air.

52. Carbon Dioxide Generator. Place several lumps of marble in the bottom of a bottle or flask (see Fig. 8) fitted with a two-holed rubber stopper. Through one hole is inserted a thistle tube which reaches quite to the bottom of the generating flask, where it is sealed air- or gas-tight when

a little liquid is poured into the flask. Through the other hole of the stopper passes a delivery tube and this tube is prolonged so that it reaches below the surface of the water in the trough where are placed inverted bottles filled with water ready for collecting the gas.

It will be recollected that this method of displacing water from inverted bottles immersed in a trough of water was

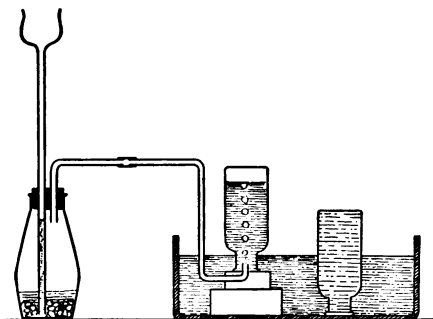


FIG. 8. — Carbon Dioxide Generator. Cracked marble is placed in generator flask. Enough water is added to close the lower end of the thistle tube. Then hydrochloric acid is added a little at a time to obtain a moderate flow of the gas.

also used for collecting oxygen. This is in fact the usual method of collecting gases, and may be used for any gas that is not very soluble in water.

Now with the generator and connections all arranged a little water is poured into the thistle tube until its lower end within the generator

is submerged and thus sealed so that no gas can escape this way. Then concentrated hydrochloric acid is added, a few drops at a time, until a fairly brisk effervescence takes place in the flask.

The first gas to issue from the delivery tube should be rejected because it is mixed with the air that was originally in the generator, but after considerable gas has escaped, the air will all have been swept from the generator and pure carbon dioxide can be collected by sliding the inverted bottles of water over the end of the delivery tube.

PROPERTIES OF CARBON DIOXIDE

53. Specific Gravity. Accurate experiments have shown that carbon dioxide weighs 1.529 times as much as air, in other words that its specific gravity is 1.529. It is not necessary or even desirable for every student of chemistry to repeat the somewhat elaborate experiment necessary to prove the correctness of this exact figure, which has been obtained by skillful and reliable experimenters.

A striking experiment for showing the greater density of carbon dioxide is illustrated in Fig. 9. Several lighted candles are placed in an inclined trough; then carbon dioxide, previously collected in a large cylinder, is

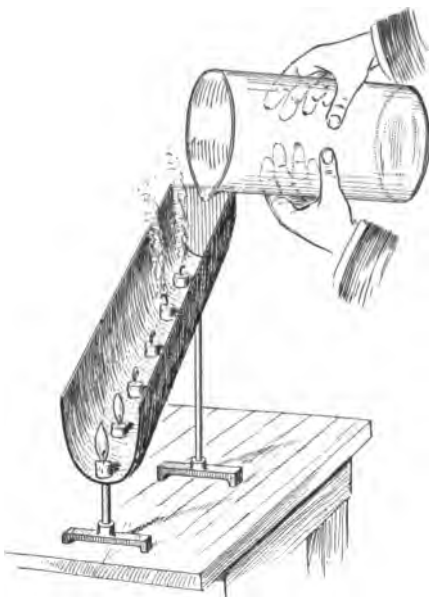


FIG. 9. — Carbon Dioxide flowing down hill.

poured into the top of the trough. It is shown by the candles becoming successively extinguished that the carbon dioxide flows down hill through the trough.

54. Solubility in Water. Carbon dioxide is not very soluble in water, as has been shown by the fact that it has been collected in bottles inverted over water. It could be shown, however, that some of the gas dissolved in the water through

which it bubbled. Close the mouth of one of the bottles of carbon dioxide inverted in the collecting trough by placing the palm of the hand under it, transfer the bottle to another trough containing fresh cold water. On letting the bottle stand in this trough a few hours, it is found that the water level within the bottle rises very considerably, showing that some of the gas has disappeared and the water risen to take its place. The only way in which the gas can disappear is by dissolving in the water.

At ordinary temperature and with the gas under the pressure of the atmosphere, a volume of water is capable of dissolving about its own volume of carbon dioxide gas. Under less pressure, less, and under greater pressure, more, gas can be dissolved. Plain soda water, more correctly called carbonated water, obtained at a soda fountain or dispensed in siphon bottles, is simply a solution of carbon dioxide in water. The carbon dioxide is forced under a high pressure into bottles or metal tanks of water, and under the high pressure a correspondingly large amount dissolves. When the carbonated water is drawn into a glass, the pressure is relieved, and we see most of the carbon dioxide escaping in the bubbles which rapidly rise.

55. Liquid Carbon Dioxide. Dry carbon dioxide gas may be liquefied by compression at the ordinary room temperature. At 20° C. a pressure of 861 pounds per square inch or, in other words, a pressure 59 times as great as that of the atmosphere, is required. Of course very strong containers are necessary to withstand this pressure, and it is customary to compress the gas into steel cylinders in which it is put on the market. Compression always produces heat, and unless the compressing apparatus and the receiving cylinder are surrounded by cold running water to carry away

the heat, the temperature will rise and liquefaction will be impossible.

56. Solid Carbon Dioxide. If the cylinder of liquid carbon dioxide is placed with the valve at the bottom and the valve is opened, some of the liquid will be forced out. But here we make the surprising observation that we do not obtain any liquid at all outside of the pressure cylinder, but we do get a solid substance which looks like snow. A good way to obtain this snow is to tie securely a stout, coarse bag over the escape pipe of the cylinder and open the valve for a few minutes. Considerable frost can be seen on the outside of the bag and the hissing of escaping gas is heard. On closing the valve and opening the bag, several handfuls of carbon dioxide snow are found.

On compressing carbon dioxide gas to a liquid, we just said that a large amount of heat is produced that has to be removed with cold water. Now on letting liquid carbon dioxide escape from the cylinder, an equal amount of heat must be supplied from somewhere if the liquid is to be changed back to a gas. Enough heat is not at once available from the liquid and its immediate surroundings, but what there is, is taken, and some of the liquid is thereby changed to gas. This withdrawal of heat produces great cold and it is thus that the remaining carbon dioxide is frozen. The temperature of the snow is as low as -60°C . It could serve thus as an excellent refrigerating agent for temperatures below that of the ordinary ice-salt mixture.

This carbon dioxide snow is a fascinating substance to handle. Holding a little lump in the palm of the hand, it may be seen to evaporate. A lump thrown into a dish of water causes the water to freeze. Mercury poured upon it at once becomes solid. In handling it, however, one must

avoid pressing it against the flesh, else it causes frostbite, the effects of which are quite similar to those of burning.

57. Chemical Properties of Carbon Dioxide. We have already seen that carbon dioxide is absorbed by limewater and produces in it a white turbidity, also that it dissolves to some extent in water.

We know that a glass of plain soda water, — that is, the carbonated water without the addition of fruit sirups, — tastes somewhat sour. Carbon dioxide, in fact, forms a weak acid with the water in which it dissolves. We shall learn more later about acids, but it is true that all acids are sour in taste. Another general property of acids is that they cause the color of a vegetable dyestuff called litmus to change from blue to red. When a piece of paper colored blue with litmus is dipped into water containing dissolved carbon dioxide, the color is changed to a rather pale red.

Another property of acids is that they react with the oxides of metals to form salts. Now limewater is obtained by allowing lime, which is oxide of calcium, to react with water. The product of the reaction is slightly soluble in water and the clear solution is known as limewater. Carbon dioxide reacting with the limewater gives calcium carbonate, a white insoluble salt which produces the milky appearance which we have described as a distinctive test for carbon dioxide.

USES OF CARBON DIOXIDE

58. Fire Extinguishers. The experiment of extinguishing the burning candles suggests one of the important uses of carbon dioxide, namely, as a fire extinguisher. The so-called automatic fire extinguishers are a familiar sight in the corridors of public buildings and in railway cars. The most useful form consists merely of a device for manufactur-

ing, when the occasion may suddenly demand it, a large amount of carbon dioxide which will charge the water in the extinguisher and at the same time create a pressure to force the charged water through the nozzle so that it can be directed at the fire. The carbonated water, on being relieved from the great pressure and moreover warmed on striking the fire, gives up a large amount of the carbon dioxide, which it can no longer hold in solution. The gas, being heavier than air, tends to spread over the fire and exclude the air. The water thrown by the extinguisher also helps to put out the fire by cooling the fuel below its kindling point, but the efficiency of one of these so-called chemical fire extinguishers is greater than if only the same amount of water were thrown.



FIG. 10. — Chemical Fire Extinguisher.

The extinguisher is usually constructed as shown in the diagram (see Fig. 11). The metal tank is filled with water nearly to the top (the level of the water is seen at *A*) and a proper quantity of some carbonate, usually sodium bicarbonate, or common baking soda, is added and allowed to dissolve in the water. Marble would be too slow in its action, but the soluble carbonate being infinitely more finely divided when in the dissolved state than the most finely ground marble dust, is much more rapidly acted upon. The amount to add would be determined by the capacity and strength of the tank. Directions always accompany the chemical extinguishers and state how much sodium bicar-

bonate and sulphuric acid to use. In the top of the tank is a support for a bottle of concentrated sulphuric acid. This

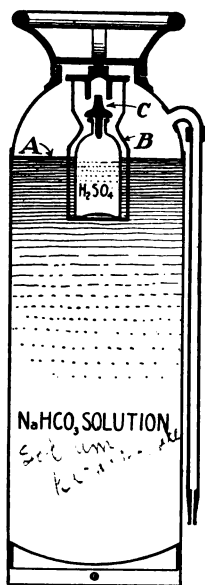


FIG. 11. — Section of Fire Extinguisher.

support (*B*) is made of some metal little likely to corrode in a damp place. The stopper of the sulphuric acid bottle (*C*) is of lead and fits loosely. The hose through which the contents of the tank are to be discharged is attached to what is the top of the tank when the latter is not in use. When occasion arises to use the extinguisher, it is taken to the scene of the fire and at once inverted. The sulphuric acid is thus emptied out into the solution of sodium bicarbonate, and rapid evolution of carbon dioxide begins. The pressure rises and the solution is expelled forcibly through the hose which leads from what is now the bottom of the tank. If the hose were not at the bottom (when in action), of course only gas would escape.

59. Soda Water. The use of carbon dioxide dissolved in water in the production of effervescing drinks has already been referred to in the paragraph on the solubility of carbon dioxide. The original *soda water* was prepared by mixing baking soda (sodium bicarbonate) in solution with some fruit acid. Carbon dioxide was produced as is the case when any acid acts on any carbonate, and the water was thus charged with the gas. But carbon dioxide is only one of the products of the action of sodium bicarbonate with an acid. The other product is a salt, the sodium salt of the fruit acid. This salt is not harmful, but it does not add to the attrac-

tiveness of the beverage. To-day soda water is universally made by charging pure water in strong metal tanks with pure carbon dioxide gas. Thus the modern soda water really contains no soda at all.

60. Raising of Bread and Cake. In making bread and cake it is essential that the product shall be light and porous, for otherwise it would be neither appetizing to eat nor easy to digest. Lightness is obtained through the agency of carbon dioxide, which is generated throughout the mass of the dough, either by the action of yeast or of baking powder, so that the dough becomes filled with a multitude of little bubbles. These bubbles "raise" the bread.

Yeast consists of a vast number of little plant cells, which grow and multiply very rapidly when put in the moist dough, and in the process of their growth cause a chemical change in the starch of the flour and in the sugars present in the dough. The final products of this change are chiefly alcohol and carbon dioxide. The amount of alcohol is so small that it is quite unnoticeable; but the carbon dioxide, being a gas, has a large volume in proportion to its weight and thus it causes the expansion of the bread.

Baking powder is made by mixing sodium bicarbonate with some dry powdered acid substance, as for example cream of tartar. So long as the baking powder remains dry no action occurs; but when it is moistened, the acid reacts with the carbonate and produces carbon dioxide gas.

The baking powder should therefore be first well mixed with the flour so that gas will be released equally in every part of the mass and the mixing of the flour with the watery materials (milk, water, or eggs) should take place just before the material is to go into the oven so as to avoid the loss of gas.

Baking soda, which is sodium bicarbonate, is frequently

used with sour milk to bring about the raising of homemade products such as griddle cakes or gingerbread. In this case, carbon dioxide is released from the sodium bicarbonate by the action of lactic acid in the sour milk. Frequently the housewife takes too much, or perhaps too little, soda for the amount of acid in the sour milk. The resulting product may then taste strongly either of the excess of soda or of acid. In making baking powder, the manufacturers are careful to properly proportion the two ingredients so that no excess of either shall be left unchanged at the end of the reaction.

61. Commercial Methods of making Carbon Dioxide.

Sulphuric acid is cheaper than hydrochloric acid, and it is therefore used in the commercial manufacture in preference to the more expensive acid which is most often used in the laboratory. With the strong effervescence, a spray carrying considerable sulphuric acid is thrown up, and therefore the gas must be passed through a washing vessel containing pure water and best also strained through some porous material before being charged into the siphons of carbonated water or liquefied into steel cylinders.

Carbon dioxide is the chief gaseous product from the fermentation of grain, and large quantities of this gas are produced in distilleries and breweries. Of late years the practice has grown not to allow this gas to go to waste, but to collect it and compress it in steel cylinders, so that to-day a large part of the carbon dioxide in use is obtained in this way.

CARBON MONOXIDE

62. Formation. In connection with our study of combustion (page 31) it was said that if carbon is burned in an insufficient supply of oxygen, a gas called carbon monoxide is

produced. The most favorable conditions for the formation of carbon monoxide exist in a deep coal or charcoal fire to which air is admitted only at the bottom. The air at the bottom doubtless burns some of the carbon to carbon dioxide. The heat of the reaction brings the layer of fuel above to incandescence, and any carbon dioxide starting to pass up through this layer of white-hot carbon reacts with it and thus becomes changed back to carbon monoxide.

63. Properties of Carbon Monoxide. Physical Properties.

Carbon monoxide is colorless and odorless. It is lighter than carbon dioxide, being a trifle less heavy than air, whereas carbon dioxide, as we have seen, is about one and one half times as heavy as air. It is very slightly soluble in water.

Chemical Properties. Carbon monoxide, unlike carbon dioxide, does not react with water to form an acid. Its most striking and useful property is its ability to take on more oxygen when burning, thus forming carbon dioxide. Carbon monoxide is excessively poisonous to breathe, even when largely diluted with air. Hence the danger from leaky furnaces and from leaking water gas (see below).

64. Uses of Carbon Monoxide. Large amounts of carbon monoxide, usually mixed with other fuel gases, are prepared and used as artificial gas for heating and lighting. For lighting, other gases must be present as carbon monoxide itself burns with a non-luminous flame. Water gas, which is a variety of illuminating gas used very largely in cities, and producer gas which is much employed as a fuel gas, both contain very high proportions of carbon monoxide.

65. Combining Proportions. Carbon dioxide and carbon monoxide are both composed of exactly the same elements, yet the two gases have very different properties, as different in fact as two gases composed of totally different elements.

The difference is to be accounted for only on the ground of the difference in the proportion of the two elements combined.

In carbon monoxide one gram of carbon is combined with 1.333 grams of oxygen. In carbon dioxide one gram of carbon is combined with 2.666 grams of oxygen. The remarkably simple relation is at once perceived — that for a given amount of carbon (one gram in each of the above cases) the second gas contains exactly twice as much oxygen as the first gas. Hence the name *di*-oxide, the prefix *di* coming from the Greek and meaning two. In distinction, the prefix *mono* means one.

66. Law of Multiple Proportions. Besides carbon and oxygen there are many pairs of elements which combine in more than one proportion. We have found the very remarkable fact that the two combining ratios of carbon and oxygen bear the simple relation to each other of two to one. Now it has been found that in all cases of more than a single combining ratio, the relations are of the same simple nature. A general statement of this fact is known as the Law of Multiple Proportions.

We shall see later that this law, together with the law of definite proportions, at which we have already hinted (page 22), are of the greatest significance, since they point the way to our present conception of the nature of matter, namely, to the theory of atoms.

SUMMARY

Carbon Dioxide in Nature. The amount of carbon dioxide being continually turned into the atmosphere by fires, the exhalations of animals, and decay is enormous, yet the amount present does not increase.

Green plants absorb carbon dioxide, using the carbon and returning oxygen to the air.

Large amounts of limestone, a rock which contains carbon dioxide united with the oxide of calcium, are found in nature. Some mountain ranges are composed mainly of this one kind of rock. Marble is a pure form of limestone. It readily gives up pure carbon dioxide when it is treated with an acid.

Properties of Carbon Dioxide. Carbon dioxide is colorless, odorless, and has a slight acid taste, is somewhat soluble in cold water, and becomes very soluble under high pressure. It is about one and one half times as heavy as air, it may be liquefied by pressure at ordinary temperature, and it may be frozen by the cold produced by the vaporization of the liquid.

Carbon dioxide neither burns nor supports combustion. It reacts feebly with water to form a weak acid. With limewater it reacts to form a white precipitate of calcium carbonate, and this reaction is a distinctive test for the presence of carbon dioxide.

An important use of carbon dioxide is in the chemical fire extinguisher. Dissolved in water under pressure, it is an essential constituent of carbonated beverages. When produced chemically by the action of yeast or baking powder throughout a mass of dough, it serves in raising bread and cake.

Carbon monoxide is obtained when carbon burns with insufficient oxygen. It contains the same elements as carbon dioxide, but it has very different properties. For the same weight of carbon, carbon dioxide contains just twice as much oxygen as does carbon monoxide. A relation of this kind holds for many other sets of compounds besides the oxides of carbon, and it finds general expression in the law of multiple proportions.

Questions

1. Enumerate several of the ways in which carbon dioxide is being continually turned into the atmosphere.
2. Explain how the quantity of carbon dioxide in the atmosphere is regulated by natural processes so that it is nearly constant.
3. A fragment of building stone when dropped into a test tube

containing acid effervesces and the gas given off clouds limewater. What probably is the stone?

4. Upon what three properties of carbon dioxide does its use in fire extinguishers depend?

5. How could one tell whether a gas that would not support combustion was carbon dioxide or nitrogen?

6. Why is it dangerous to health to have leaks in the fire pot of a hot-air furnace?

7. If the water of a mineral spring effervesces strongly on reaching the surface, what gas would you suspect and how would you prove the point?

8. Why is it customary to lower a lighted candle into a well before sending a man down to make repairs?

9. Explain two different methods of "raising" bread.

10. What is one of the principal fuel constituents of "water gas"?

CHAPTER VII

THE ATMOSPHERE AND NITROGEN

67. Approximate Composition of Air. We have already seen that about one fifth of the air consists of oxygen, the supporter of combustion, and that after that one fifth is used up the residual gas is inert. The residual gas consists mainly of the element nitrogen.

68. Nitrogen from the Air. If we wish to obtain fairly pure nitrogen from air, it is only necessary to exhaust the oxygen by causing it to combine with some substance with which it gives a solid oxide, for example, with iron, copper, or better, phosphorus. Charcoal would not serve the purpose, because its combustion yields a gas which would remain admixed with the nitrogen.

A jarful of nitrogen is prepared most readily as follows: Place a piece of phos-

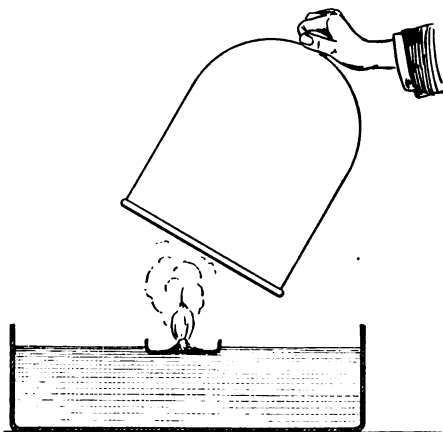


FIG. 12. — **Exhaustion of Oxygen.** Oxygen removed from air under a bell jar by means of burning phosphorus.

phorus on a porcelain crucible cover which rests on a cork floating on the surface of a large panful of water. Set

fire to the phosphorus and quickly cover it with a large glass bell jar (see Fig. 12) so that the air within the jar is sealed from the outer air by means of the water. At first the heat of combustion may cause so much expansion that a few bubbles of air will be forced out from under the sides of the jar. A very dense white smoke is formed but this should not be mistaken for a gas. It consists simply of very fine solid particles of oxide of phosphorus and after a sufficient time it settles out completely and leaves a perfectly clear gas. As the gaseous residue cools, the water is observed to rise a considerable distance in the bell jar, indicating, of course, that there is now less gas than formerly.

If enough phosphorus was taken at the outset in the above experiment, it is now observed that some of it remains unburned; if any other burning material is now introduced into the residual gas, it is extinguished, showing that the gas is a non-supporter of combustion. When we first found that combustible substances burn better in pure oxygen than in air, we at once assumed that, mixed with the oxygen of the air, there was another gas which was a non-supporter of combustion. We have now shown that this assumption is correct.

69. Preparation of Pure Nitrogen. The nitrogen obtained by removing oxygen from air has small quantities of other gases mixed with it, since the phosphorus removes only the oxygen. Pure nitrogen is usually prepared by heating a concentrated solution of ammonium chloride and sodium nitrite. The gas is collected in bottles by water displacement.

70. Properties of Nitrogen. On testing the gas in the bottles, it is found that it neither burns nor supports com-

bustion. In this respect it resembles carbon dioxide, but it differs from that gas in that it does not cloud limewater. Nitrogen is a little lighter than air, having a density, at standard conditions, of 1.25 grams per liter. Nitrogen is only half as soluble in water as oxygen is. 100 volumes of water under usual conditions, dissolve about 1.6 volumes of nitrogen.

71. Air a Mixture. The difference in solubility of the two chief components of the air furnishes a strong reason for believing that air is a mixture and not a chemical compound of oxygen and nitrogen. If water which has been standing in contact with the air is boiled and the dissolved air thereby expelled is caught and analyzed, it is found to contain 34 per cent of oxygen, whereas atmospheric air contains but 21 per cent. If air were a chemical compound, it would be dissolved as a whole and afterwards on removal from the solution its composition would not be changed.

We shall see in a later chapter that there are several distinct compounds of oxygen and nitrogen, the properties of which are radically different from each other and from either of the uncombined elements. On the other hand, air shows the properties of both oxygen and nitrogen, only modified to the extent to which these components are diluted with one another. Thus in this respect also air shows the characteristics of a mixture.

Furthermore, oxygen and nitrogen can be mixed and the mixture at once shows the properties of air, although no evidence of chemical reaction, such as evolution of heat, is to be observed. The mixture indeed can be made in proportions other than those existing in air and yet the properties are not essentially different. If air were a chemical compound, its composition would be unalterable.

72. Inertness of Free Nitrogen and Importance of Combined Nitrogen. The above described simple experiments with the bottle of nitrogen have shown that nitrogen is a very inert gas. Nitrogen can, however, enter into chemical combination, and many important compounds, including ammonia and nitric acid, are formed from it. Nitrogen is an essential constituent of all living organisms; indeed human food is judged largely according to the percentage of chemically combined nitrogen which it contains; and soils and fertilizers are of value as plant foods largely in proportion to the amount of chemically combined nitrogen which they contain. In spite of the great importance of nitrogen in the chemistry of living things, the atmospheric nitrogen plays almost no direct part in the nutrition of animals and plants. This fact further emphasizes the inert nature of this element when it is in the uncombined state. Of the air that men and animals breathe, it is only the oxygen that is utilized; the nitrogen is entirely exhaled again.

73. Nitrogenous Foods. All the nitrogen for our nutrition enters our bodies as combined nitrogen in our food. Meat and fish foods, milk and cheese, beans and peas and mushrooms, contain a considerable proportion of combined nitrogen; most grains and vegetables contain less. The gluten of wheat, which comprises some twelve to fifteen per cent of the weight of the whole wheat, is a nitrogen-containing food, and it is largely due to the quantity of gluten that wheat is so highly prized as a food.

Just as animals are compelled to take the nitrogen that they need in the combined form, so plants obtain theirs from the soil in the form of soluble nitrogen compounds which are taken up with the water of the soil through their roots. It

is on account of the nitrogen which it contains that slaughter-house refuse is valuable for fertilizer.

74. Fixation of Nitrogen by means of Legumes. There are a few plants, namely, those of the legume family, of which beans, peas, and clover are members, which are able through the agency of colonies of bacteria which live on their roots, to obtain a certain amount of atmospheric nitrogen by causing it to enter chemical combination. It is on this account that when a field is exhausted of its nitrogenous material by long cultivation, the farmer plants it with clover to restore its fertility.

75. Artificial Methods of Causing Nitrogen to Combine. We have seen that the natural means of "fixing nitrogen," as it is called, that is, of causing the inert gas of the air to enter chemical combination, in which state it is available for nutrition, are very limited. Within recent years artificial means have been developed, and now the fixation of nitrogen directly from the air, for use as a fertilizer, is becoming an industry of importance. Indeed, this industry promises to increase to a very great extent.

One of the most important of the artificial methods depends on a fact discovered by Cavendish as long ago as the latter part of the eighteenth century. He passed electric sparks through a confined volume of air and found that the "air" would then dissolve in small amount in water to form an acid (nitric acid). Under the influence of the electric spark nitrogen and oxygen combine to form nitric oxide. This oxide of nitrogen is a chemical compound; it is no longer a mixture of oxygen and nitrogen, but an entirely new substance with entirely new properties. The important new property from the standpoint of this process is that it unites readily with water and more oxygen to form nitric acid.

For use as a fertilizer the acid is treated with limestone whereby calcium nitrate is obtained. .

A large amount of electrical energy is expended in effecting this chemical combination of nitrogen, and it is therefore only near great waterfalls, where power is abundant, that this process has a chance of success. Niagara Falls being in a thickly settled district where the demand for power is great, the price is not as low as one might expect from the magnitude of the supply. Norway possesses great waterfalls where electric power is developed so cheaply that the manufacture of nitric acid and nitrates from the air is proving a distinct commercial success.

76. Carbon Dioxide and Water Vapor in Air. Oxygen and nitrogen constitute the main bulk of the atmosphere, and they are perhaps the most important constituents of the air; but there are two other constituents which are of exceedingly great importance, namely, carbon dioxide, which is only present to the extent of three or four volumes in 10,000 volumes of air, and water vapor, which is present in variable amount according to atmospheric conditions, but rarely exceeds 2 per cent of the whole.

77. Argon. In addition to these gases, there is still another, whose presence was not even suspected until 1894. It is of no practical importance, but it is of very great interest on account of the fact that it constitutes nearly 1 per cent of the air and yet it remained so long undiscovered.

If the residual part of the air from which oxygen has been extracted is subjected to the action of magnesium and the electric spark, the nitrogen combines to form magnesium nitride. When this is done there is always left a small amount of gas, amounting to about 1 per cent of the air taken at first. This fact was observed by Cavendish, who

noticed that whenever he attempted to remove all the oxygen and nitrogen from a confined volume of air, a small bubble of gas always remained. Cavendish observed this fact, but paid little attention to it, probably thinking that the gas remaining was some nitrogen which had not been completely removed. Indeed, this residual gas shows the same general property of inertness as nitrogen. It thus escaped serious attention until 1894. In that year Lord Rayleigh, an English physicist, made accurate measurements of the density of nitrogen and other gases. He observed that the result with nitrogen obtained from air was different from that with nitrogen obtained by decomposing a chemical compound of nitrogen. The fact was then recalled that a residue was always left when the nitrogen residue of air was sparked with magnesium, and Rayleigh concluded that there must be another, previously unsuspected, gas in the air. Rayleigh was not a chemist and did not feel competent to carry the study of the problem further; he therefore enlisted the aid of the noted chemist, Sir William Ramsay, who after extensive study confirmed the discovery of another constituent of the air, and declared further that this gas was a new element. It was named argon, meaning inert.

Argon constitutes about 1 per cent by volume of the air. Besides argon, Ramsay discovered four other new gases, helium, neon, krypton, and xenon which, however, are present in the air in exceedingly minute quantities.

The most remarkable property of argon, as well as of the four other more recently discovered gases, is that of absolute chemical inertness. These gases can be made to combine with no other element, and this accounts for their being so long undiscovered and mistaken for a slight residue of inactive nitrogen. Physically, argon is not very different

from nitrogen. It is colorless, odorless, and tasteless; it is heavier than nitrogen, which fact, as we have seen, led to its discovery; its boiling point is higher than that of nitrogen and lower than that of oxygen.

ACCURATE DETERMINATION OF THE VOLUME PER CENT OF OXYGEN IN AIR

78. In order that an accurate knowledge of the composition of the air may be obtained, a much more careful method of removing the oxygen must be employed than that described in the first part of this chapter. There, it will be remembered, it was difficult to prevent the escape of some of the confined gas in consequence of the expansive effect of the heat of the burning phosphorus.

To carry out an analysis of the air, it is necessary to start with an accurately measured quantity, to remove all of the oxygen while care is taken to lose none of the nitrogen, and, finally, to measure the volume of the residual gas. The final volume is, of course, the sum of the volumes of the nitrogen and argon. The quantity of carbon dioxide — only $\frac{3}{100}$ of 1 per cent of the whole — is so small as to be negligible. The water vapor in the air may also be neglected if the volumes measured are all uniformly confined over water.

Let us now follow out step by step the course of an actual analysis of air such as we might perform in the chemical laboratory.

A narrow cylindrical glass tube which holds 100 c.c. and which is graduated to tenths of a cubic centimeter is used to contain and to measure the air. The cylinder is inverted and its open end is sunk beneath the surface of a deep body of water in a tall glass jar. A definite volume of air is thus confined in the measuring tube. If a few

cubic centimeters of water are poured into the cylinder before inverting it, the air volume will not reach to the lower end of the tube, but its boundary will come where it can be seen behind the graduations. The tube is now raised or lowered until the water levels inside and outside are the same. There is thus no pressure on the gas due to difference in water level. If there were any such difference, it would have to be taken into account; therefore it is simpler to bring the levels both to the same point and thus avoid the complication. The volume is noted as 95.9 c.c. At the same time the atmospheric pressure is noted as 778 mm. of mercury, and the temperature as 21° C. The necessity for the latter readings will appear a little later. Now that the definite amount of air is measured, we proceed to remove the oxygen by inserting from underneath a piece of yellow phosphorus attached to a bent piece of slender wire (Fig. 13). This wet phosphorus does not take fire in the tube, but it does combine slowly with oxygen and if time enough is allowed, it removes the oxygen as completely as if it had flamed up in rapid combustion. It is therefore necessary to leave the whole apparatus over night. The next morning it is extremely probable that the oxygen has

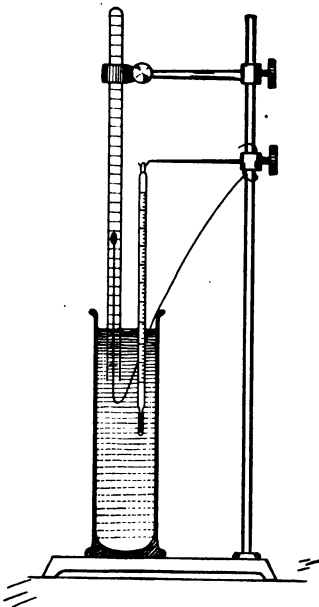


FIG. 13. — Measurement of Volume Per Cent of Oxygen in Air.

been completely exhausted. The remaining lump of phosphorus is removed and the readings taken as before. They



FIG. 14. — **Barometer.** The pressure of the atmosphere on the surface of the mercury in the cup counterbalances the weight of the column of mercury in the tube. The height of the top of the mercury surface in the tube above the free surface in the cup thus measures the pressure of the atmosphere. The scale and measuring device is not shown in the figure.

are: volume, 77.2 c.c.; pressure, 756 mm.; and temperature, 18° C. To prove, now, that no oxygen is left in the tube, a fresh piece of phosphorus, which will act more vigorously than the old piece, should be inserted and allowed to stand an hour or two. This is then removed and the volume is again read and found to be 77.2 c.c. This reading, being the same as the second, shows that no oxygen has been absorbed by the second piece of phosphorus. The thermometer and barometer are again read and found to be 18 degrees and 756 mm., respectively, not having changed since the previous reading. (If they had changed a little, it might have caused some slight change in the volume of the gas not due to further absorption of oxygen.)

Since we are compelled to leave the experiment over night, a complication arises which would not bother us if all the readings could be taken at about the same time. The volume of any gas changes with changes of temperature and pressure. Now the temperature of the gas we are interested in will probably not be the same the next day as at the time when the experi-

ment was started; neither will the pressure of the atmosphere upon the water in the deep jar (and hence on our air which is confined above the water) be the same the following day. Hence the necessity of noting the temperature and pressure at the time of each reading of volume. The temperature may be found by hanging a thermometer in the water, if the latter has been drawn long enough to come to the temperature of the room. The pressure of the air is found by reading the barometer (see Fig. 14).

In making our calculations, of the composition of the air, it will not do to subtract the 77.2 c.c. from the 95.9 c.c. and claim that 18.7 c.c. of oxygen were removed, for the temperature and the pressure both changed between the readings. We must first learn what effect change in temperature and in pressure have upon the volume of a gas and then correct the observed volumes for these changes. The next chapter is devoted to the effect of conditions on the volume of gases.

SUMMARY

Components of Air. The air is a physical mixture of several gases, of which about one fifth by volume is oxygen and nearly all of the other four fifths is nitrogen.

About one per cent of the air consists of argon, an absolutely inert gas. Besides argon, there are four other similarly inert gases in very minute amounts.

Air contains a small amount of carbon dioxide, but this small component is of very great importance.

Water vapor is present in the air in varying proportions, but rarely exceeding two per cent. Its presence is of great importance.

Nitrogen an Important Plant Food. Nitrogen is very inert chemically and can be made to combine with other elements only with difficulty. All plant and animal life requires nitrogen for its nutrition, but, with the exception of plants of the

legume family, which get nitrogen from the air by the aid of colonies of bacteria growing on their roots, all plant and animal life is compelled to use nitrogen that is already in the combined state. Combined nitrogen is, therefore, an essential constituent of fertilizers. Meats and fish, cheese and milk, beans and peas, and to some extent grains and vegetables, supply us with the necessary nitrogen in our foods. Artificial methods of causing the atmospheric nitrogen to combine are assuming commercial importance in connection with the manufacture of nitrogenous fertilizers.

Questions

1. Why is air considered a mixture rather than a definite chemical compound? Give facts which show this, other than those mentioned in Section 71.
2. Name in the order of their abundance the gases present in the air.
3. Discuss the relative importance of these gases.
4. Explain why the fixation of nitrogen is difficult, but of great importance.
5. Describe processes by which atmospheric nitrogen is in nature brought into a state of combination.
6. Describe artificial methods of accomplishing the same thing.
7. Give three methods by which oxygen can be removed from the air.
8. Why would it be advantageous from the standpoint of economy of heat to use pure oxygen rather than air in burning coal under boilers? Why is pure oxygen not thus used at present?
9. When meat is excessively high priced, what substitutes which would furnish nearly or quite as much available nitrogen might be used as food?
10. Why do farmers plant clover or alfalfa on fields which have become exhausted from frequent raising of wheat?

CHAPTER VIII

THE GAS LAWS

79. It is a familiar fact that air and other gases expand when heated and contract when cooled. The expansion of the air over the torrid zone and the resulting trade winds is an example familiar from the study of geography. A similar phenomenon on a small scale is observed in the rise of hot air over a radiator.

The expansion and contraction of air may be readily demonstrated if a flask is closed with a one-holed rubber stopper and through the latter is passed a narrow glass tube in the middle of which a short column of colored liquid is caught so as to indicate the boundary of the definite volume of confined air. The air expands even with the slight warmth imparted by holding the hands against the sides of the flask, and the thread of liquid is seen to move up in the tube. On the other hand, the volume of air contracts if the flask is cooled, and the thread of liquid can be seen to move downward. Exactly the same behavior is observed if the flask is filled with any other gas in place of air.

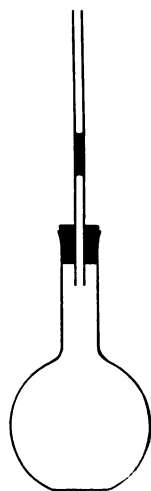


FIG. 15.—Gas Volumes change with Temperature.

80. Measurement of Temperature; Centigrade Scale. In all scientific work, temperature is measured by a scale known as the centigrade scale. This scale possesses two

fixed points which are very easy to duplicate; namely, the temperature of melting ice and the temperature of the steam from water boiling under a pressure equal to the average atmospheric pressure at sea level. The first point is called zero degrees and the second point is called 100 degrees; and the interval between these two points is divided into 100 parts (hence the name centigrade, from the Latin, indicating that the scale is graduated into one hundred parts). By extending spacings of equal lengths below 0 degrees and above 100 degrees, the centigrade thermometer is made to read over all ranges of temperature.

81. When it is wished to express the quantity of a gas in terms of its volume, it is clearly necessary to state the temperature of the gas at the time the volume was measured. One liter of a gas at 100° C. would have a different weight from one liter of the same gas at 0° C.

If gases were not so difficult to weigh, we might perhaps always express the quantity of a gas by weight; but on account of the extreme lightness of gases, it is difficult to weigh them accurately. It is, however, very easy to measure the volume of a gas.

It has been found that for all gases the change in volume for change in temperature is regular, namely, for an increase of 1° C. the increase in volume is equal to $\frac{1}{273}$ of the volume at 0° C., or for a decrease of 1° of temperature, the decrease is likewise $\frac{1}{273}$ of the volume at 0° C. This uniformity in the rate of change was first noted by Charles, in 1787, and his name is now given to the law which connects the change of volume with the change of temperature.

82. **Absolute Zero.** Before we take up the study of the application of Charles' law, it will be necessary to consider briefly the matter of *absolute temperatures*, since the modern

treatment of Charles' law makes use of the absolute scale of temperature. Let Figure 16 represent a vessel filled with a gas at 0°C . Suppose the piston with which the top is closed to be gas-tight and to slip up and down without friction. If, now, the gas is cooled by 1°C ., the volume, according to the rule just stated, will decrease $\frac{1}{273}$, and the piston will sink to a position shown by the first dotted line. If it is again cooled by 1°C ., that is to -2° , the volume will again be diminished by an amount equal to $\frac{1}{273}$ of its volume at 0°C ., and the piston will sink to the second dotted line. It can readily be seen that when the temperature has been decreased to 273 degrees below zero, the volume will have decreased to zero if the same regularity in behavior has continued. This value, -273 degrees centigrade, has a great theoretical importance and it is what is known as the absolute zero of temperature.

83. The absolute scale of temperature is graduated in degrees which are equal to those on the centigrade thermometer, but the zero point is 273 degrees lower than that of the centigrade scale. This being the case, it is necessary, whenever we wish to convert

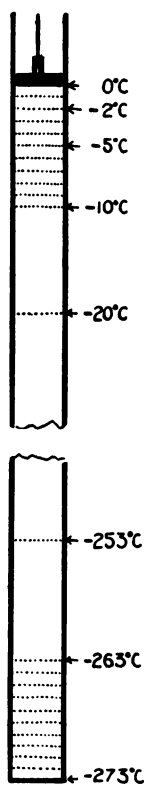
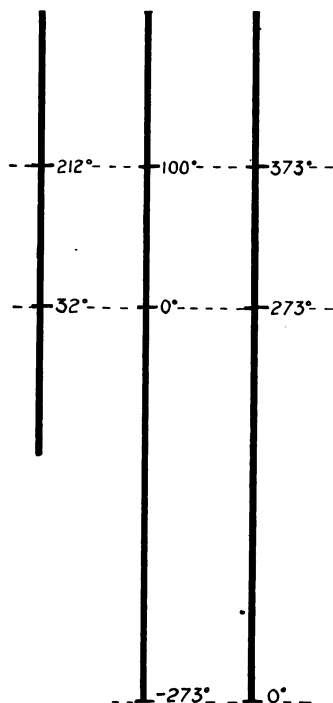


FIG. 16. — Showing Change of Volume of Gas with Changing Temperature. The volumes marked off on the lower part of the cylinder show the behavior of the ideally perfect gas. Of course no actual gas conforms perfectly to this ideal at very low temperatures although helium comes fairly near to it.

a centigrade reading into absolute, to add 273 degrees to the centigrade reading. The adding must be algebraic in



FAHRENHEIT CENTIGRADE ABSOLUTE

FIG. 17. — Comparison of Different Thermometric Scales.

order to take account properly of any minus readings. For example, to change 20° centigrade to absolute, $20 + 273 = 293$. Hence 20° C. equals 293° absolute. Again, to change -20° C. to absolute: $-20 + 273 = 253^{\circ}$ absolute. That is, if the absolute zero is 273 degrees below the centigrade zero, and if the temperature -20° C. is 20 degrees below the centigrade zero, then -20° C. is 253 degrees above the absolute zero.

84. Charles' Law. Now if any volume of gas — say, for the sake of convenience, 273 c.c. — were taken at 0° C., which equals 273° absolute, and cooled, say

10° , to 263° absolute, then, according to the rule previously mentioned, it would shrink by $\frac{10}{273}$ of its volume at zero, or in this case by $\frac{10}{273}$ of the 273 c.c. which we chose for convenience to take. Hence the new volume would be

$$\begin{aligned} & 273 \text{ c.c.} - \left(\frac{10}{273} \text{ of } 273 \text{ c.c.}\right) \\ &= 273 \text{ c.c.} - 10 \text{ c.c.} \\ &= 263 \text{ c.c.} \end{aligned}$$

It will be noticed that the new volume in this case numerically equals the new temperature on the absolute scale. If some volume other than 273 c.c. had been taken, the new volume would not have equaled the new temperature numerically, but a simple proportion would have existed between the two temperatures and the two volumes; hence a simple statement of the law of the effect of temperature on gas volumes, in terms of the absolute temperature, is as follows:

If the pressure upon a gas remains constant, the volume varies in direct proportion to the absolute temperature.

The law in this form will be found simpler to use in calculating corrections of gas volumes than in the form which states that the change in volume per one degree change in temperature is $\frac{1}{273}$ of the volume at 0° centigrade.

85. Example of a Calculation based on Charles' Law. In the experiment to determine the per cent of oxygen in air (Chapter VII, p. 74), there were 95.9 c.c. of air in the gas measuring tube at the start. The next day, after the phosphorus had taken out the oxygen, there were 77.2 c.c. of residual gas. The temperature at the time the first reading was taken was 21° C. The next day, when the volume was read, the temperature was 18° C. To make a fair comparison between the two volumes they must either be brought to the same temperature, or, what is more easily done, be calculated to the same temperature by the use of Charles' law. Let us change the first volume to the volume it would occupy at the temperature of the final reading. We will first change the centigrade readings to absolute: $21 + 273 = 294$; $18 + 273 = 291$. "The problem then becomes: the volume of the gas is 95.9 c.c. at 294° absolute. What will be the volume at 291° absolute?" According to Charles' law the volume varies directly as the absolute temperature, that is,

the two volumes and the two temperatures are in simple proportion.

Then
$$\frac{95.9}{x} = \frac{294}{291}$$

where x stands for the new volume. Multiplying the means and the extremes of the proportion, we have:

$$294 x = 95.9 \times 291 = 27907$$

whence
$$x = \frac{27907}{294} = 94.9$$

which is the number of cubic centimeters in the new volume.

We now might subtract the 77.2 c.c. of residual gas from the 94.9 c.c. to find how much oxygen had been removed, provided only that the pressure on the gas had remained constant over night, but the pressure did not remain constant. We shall, therefore, need to consider how changes of pressure affect the volume of a gas.

86. Effect of Pressure on Volume; Boyle's Law. It is a fact well known to all who have used a bicycle pump that air decreases in volume under increased pressure, and that it increases in volume if the pressure is diminished. It has been found by accurate measurements that *if the temperature is kept constant, the volume of a definite quantity of gas varies in inverse proportion to the pressure.* This rule holds for all gases, and it is known as Boyle's law.¹

Illustration of Boyle's law: If the pressure upon one liter of gas in a cylinder with an air-tight piston is doubled, the volume decreases to one half liter. If, on the other hand,

¹ For accurate work at extremely high pressures, this law does not hold strictly true; neither does the law of Charles hold strictly true under all conditions; nevertheless, for all ordinary purposes these two laws may be regarded as correct.

the pressure is lowered to one half its initial amount, the volume increases to two liters.

87. To return, now, to the calculations of our experiment on the volume composition of air, we found on page 84 that the 95.9 c.c. of air with which we started would have had a volume of 94.9 c.c. at the temperature of the final measurement; but we did not take into account the change of pressure. That we must do. The pressure as read on the barometer on the first day was 778 mm. and on the second day it was 756 mm. It is therefore necessary to correct the 94.9 c.c. for the change of pressure from 778 mm. to 756 mm. in order to find what volume the air originally taken would have had, if it had been measured under the same conditions as the residual gas. The calculation is as follows:

$$\frac{94.9}{x} = \frac{756}{778}$$

whence, multiplying means and extremes:

$$756 x = 94.9 \times 778 = 73832$$

and

$$x = 73832/756 = 97.7$$

Therefore the new volume is 97.7 c.c.

We have now calculated our initial air volume to the same conditions¹ as those of the residue, and we can subtract the volume of residue from that of air to find the volume of oxygen removed by the phosphorus.

$$97.7 - 77.2 = 20.5$$

¹ In all of these measurements the gases are measured over water and hence are saturated with water vapor. The amount of water vapor present is nearly the same in every case if the measurements are all made at about room temperature, and hence the errors due to neglecting it very nearly compensate each other. (See footnote on page 86.)

Thus 20.5 c.c. of oxygen have been removed. Next to find the volume per cent of oxygen divide 20.5 by 97.7. The quotient is 0.210 and thus 21.0 per cent by volume of the air is shown to be oxygen. This result is of approximate accuracy and a result obtained by this method should not vary by more than 0.2 of one per cent from the true value.

88. Standard Conditions. We most frequently use Charles' and Boyle's laws for the purpose of changing from ordinary conditions of temperature and pressure to 0° C. and 760 mm. These are called *standard* temperature and *standard* pressure and together are often spoken of as *standard conditions*.¹

The standard temperature is chosen and agreed upon by all scientific workers as 0° C. because this is the temperature of melting ice and is the most easily and accurately obtainable temperature.

The standard pressure is taken as 760 mm. of mercury because that is found to be the average pressure of the atmosphere at sea level.

89. Calculations to Standard Conditions. The weight per liter of all gases at standard conditions has been very carefully determined; and in most cases, when we wish to know the weight of any gas that we may collect, we measure its volume, take its temperature and pressure and calculate

¹ The weight of a gas at standard conditions always refers to dry gas. If the gas is collected over water at room temperature and atmospheric pressure, it will occupy between two and three per cent more volume than if it were collected dry. In connection with the study of this chapter, the student is recommended to ignore the possible presence of water vapor.

For those who have time to study the matter or the necessity for so doing, the method for correcting for the presence of water vapor is outlined on page 426, in the Appendix.

what volume it would have at standard conditions and then calculate its weight by comparing its volume with the unit volume (the liter) whose weight is known. The method of calculating to standard conditions is precisely similar to that for calculating to any other conditions. The volume varies directly with the absolute temperature and inversely with the pressure.¹

For example — let the observed volume be 45.0 c.c., the temperature, as read, be 20° C., and the pressure be 740 mm. The gas may be supposed to be dry in this case. If it were wet, a further correction would be necessary in accurate work, as the water vapor has a pressure of its own which has to be taken into account. We wish to find the volume at 0° C. and 760 mm. The steps in the calculation are (correcting first for the temperature change):

$$\frac{45.0}{x} = \frac{273 + 20}{273 + 0} = \frac{293}{273}$$

then, multiplying means and extremes, we have

$$293 x = 45 \times 273$$

whence, dividing through by 293, we have

$$x = \frac{45 \times 273}{293}$$

We might perform the indicated operations and thus find the numerical value of x , which would be the new volume after the temperature change; but we do not care to know that, but rather the volume after both temperature and pressure have changed. We can therefore let $\frac{45 \times 273}{293}$

¹ See previous footnote.

stand for the present volume and correct it further for pressure as follows:

$$\frac{45 \times 273}{\frac{293}{x}} = \frac{760}{740}$$

Multiplying means and extremes, we have

$$760 x = \frac{45 \times 273 \times 740}{293}$$

and dividing through by 760, we have

$$x = \frac{45 \times 273 \times 740}{293 \times 760}$$

The problem is now in form for numerical solution. The use of logarithms or of the slide rule will be of great assistance in performing the indicated operations at this point.¹ If the pupils are not acquainted with logarithms or the slide rule, the longer arithmetical method will have to be followed.

Performing the indicated operation, $x = 40.8$; thus we see that the volume would be 40.8 c.c. at standard conditions.

Throughout this chapter it has been assumed that the levels of the liquid over which the gas has been collected are alike inside and outside the gas measuring tubes. In case this is not true, a further correction must be applied to the calculation or else the levels must be made alike. In most cases, the latter is the easier thing to do.

SUMMARY

Charles' Law: If the pressure remains constant, the volume of any gas varies *directly* as the absolute temperature. In other words, the first volume is to the final volume as the first temperature is to the final temperature, or

$$\frac{\text{first volume}}{\text{final volume}} = \frac{\text{first temperature}}{\text{final temperature}}$$

¹ For table of logarithms, see Appendix.

whence, final volume = first volume $\times \frac{\text{final temperature}}{\text{first temperature}}$

Boyle's Law: If the temperature remains constant, the volume of any gas varies *inversely* as the pressure. In other words, the first volume is to the final volume as the final pressure is to the first pressure, or

$$\frac{\text{first volume}}{\text{final volume}} = \frac{\text{final pressure}}{\text{first pressure}}$$

whence, final volume = first volume $\times \frac{\text{first pressure}}{\text{final pressure}}$

Combined Laws: When both the temperature and pressure are varied at the same time, the combined laws may be expressed as follows:

$$\text{final volume} = \text{first volume} \times \frac{\text{final temperature}}{\text{first temperature}} \times \frac{\text{first pressure}}{\text{final pressure}}$$

Questions

1. What will be the final volume if 25 c.c. of gas at 20° C. is warmed to 30° C. at constant pressure? *increased*
2. If 50.0 c.c. of gas at 30° C. is cooled to 20° C.? *decreased*
3. If 45.0 c.c. of gas at 24° C. is cooled to 0° C.?
4. If 50.0 c.c. of gas at - 10° C. is warmed to 0° C.?
5. If 100.0 c.c. of gas at 0° C. is heated to 546° absolute?
6. The temperature remaining constant, calculate the final volume if the pressure on 200 c.c. of gas at 740 mm. is changed to 760 mm.
7. If the pressure on 100.0 c.c. of gas at 780 mm. is changed to 760 mm.
8. If the pressure on 40.1 c.c. of gas at 740 mm. is changed to 780 mm.
9. If the pressure on 20 c.c. of gas at 780 mm. is changed to 740 mm.
10. What will be the final volume if 100 c.c. of gas at 760 mm. are compressed under 1520 mm. pressure?

11. A given amount of gas measures 100 c.c. at 20° C. and 740 mm. What will be the volume under standard conditions, that is, at 0° C. and 760 mm.?

12. Correct the volume of 50 c.c. of gas at 30° C. and 745 mm. to standard conditions.

13. Correct the volume of 55 c.c. of gas at -10° C. and 780 mm. to standard conditions.

14. A given amount of gas measures 55 c.c. at -10° C. and 780 mm. What is its volume at 10° C. and 740 mm.?

15. A certain volume of gas at 0° C. and 760 mm. has its temperature raised until its volume is doubled, and then the pressure raised until its volume is brought back to the original value. What are the final conditions of temperature and pressure?

CHAPTER IX

WATER

90. Properties of Water. Water is universally known as a colorless, odorless, tasteless, mobile liquid. There are a great many liquids besides water, however, and many of them are colorless, many are odorless, and some are tasteless. So it appears that even so common a substance as water might be confused with some other substance unless its properties were accurately known. The statement that has already been made applies well here: that the properties of a substance are absolutely constant. Hence, once knowing accurately the properties of water, we may be certain that any liquid that has exactly the same properties is also water, but that any liquid that shows any properties different from those of water is not water.

It would take a good many pages to describe fully all of the properties of water, and we may content ourselves with a few of the most striking ones which are most useful in distinguishing it from other substances.

Water is a liquid at ordinary temperatures. At a certain definite temperature, 0° C., it solidifies to a form that we know as ice; at 100° C., at the ordinary atmospheric pressure, it boils, whereby it is converted into a gas that fills many times the volume (in round numbers 1700 times) that is occupied by the water as a liquid. This gas is known as steam; it is colorless and transparent, but if it escapes into the cold air, it condenses into droplets of liquid water which produce a cloud or mist.

91. Water as a Solvent. Water has the power of dissolving many substances ; for example, a substance like sugar when put into water goes into the water and mixes uniformly with it, thereby becoming a part of the liquid, which is now a solution of sugar in water. This power of water to dissolve other substances renders it useful for cleaning purposes. It is also of supreme importance in connection with the digestion and assimilation of food in the body. Most chemical changes in the practical work of the manufacturing chemist, as well as most of those that we meet with in the laboratory, take place in water solution. Hence the solvent power of water is of great importance.

Limit of Solubility. On testing the power of water to dissolve different substances, it is found that there is a definite limit to the amount of a substance that a given amount of water will dissolve at a given temperature. This limit is different for each different substance. For example, 100 grams of water at 25° C. will dissolve 37 grams of saltpeter (potassium nitrate), 35 grams of common salt, and only 5 grams of boric acid. There is a wide range of solubility among the many different substances that will dissolve in water.

Change in Solubility with Change in Temperature. In general, the higher the temperature the greater the solubility of solid substances in water. Thus 100 grams of water at 100° C. will dissolve 246 grams of saltpeter, 40 grams of salt, and 27 grams of boric acid. It will be noted that common salt gains but little in its solubility at 100° C. over that at 25° C. A few substances, among them calcium hydroxide (slaked lime), become less soluble as the temperature increases.

92. Water in Chemical Life Processes. Its power to dissolve other substances makes water essential in the chemistry

of the life processes of plants and animals. Food in the course of digestion is transformed into soluble compounds which pass in solution through the membranes of the digestive tract into the blood, and by the blood are carried to the various parts of the body, where they undergo further reaction in the formation of muscular tissue, bone, and other tissues.

Water plays an equally important part in plant life. Nitrogen-containing substances and mineral substances necessary for plant nutrition are in solution in the water in the soil and are sucked up by the roots of plants. Plants, to be sure, draw a considerable part of their nutrition from the carbon dioxide of the atmosphere. This reacts with water in the cells of the green leaves and forms sugar-like substances which are conveyed in the sap to the growing parts of the plant. Thus water is absolutely essential to all the chemical processes taking place in animals and plants

93. Irrigation. Some of the deserts in our great West which were formerly absolutely barren of any useful vegetation are now, through irrigation, among the most fertile lands of the country. The necessary food materials were in the soil, but lacked the solvent power of water to make them available for plant life.

94. Atmospheric Moisture, Humidity, and Precipitation. The greater part of the cultivated land depends upon the rain for its moisture. Even when the land is irrigated, the water comes from rivers which are supplied by the rain and snow that fall on the mountains. So the ability of the atmosphere to contain water vapor is essential to the existence of life.

It is a well-known fact that wet clothes are hung out to dry. The water evaporates and becomes a part of the air.

Likewise the water of the ocean evaporates and the moisture is carried by the wind over the land. Now the amount of water which can evaporate into a given space depends only on the temperature and varies very greatly with change in temperature. At 0° C. one cubic meter (about 1.3 cubic yards) of space can take up nearly 5 grams of water vapor; at 20° C. or approximately room temperature, 17 grams, at 30° C. or warm summer temperature, 30 grams; at 40° C. or excessively warm summer temperature, 52 grams.

Relative humidity is a term used in reporting atmospheric conditions. When the air contains the maximum possible water vapor at the given temperature, it is saturated and its relative humidity is 100 per cent. With lesser amounts of moisture, it is unsaturated and its humidity is expressed in per cent of the saturation value for that temperature.

Precipitation occurs when the air becomes supersaturated with moisture. This can occur when nearly saturated warm air becomes cooled. Its capacity for water vapor is much lower at the lower temperature and so what will only saturate at the higher temperature will more than saturate the air at the lower temperature. Therefore the excess above the saturation point precipitates as mist or rain. Water vapor is entirely invisible. For example, the average schoolroom contains one kilogram or about two pounds of water as invisible vapor. Likewise, the air on a perfectly clear day may contain large amounts of water vapor. If the air currents become cooled, mist and clouds are formed. Mist consists of a vast number of very small globules of liquid water, which are so small that they remain suspended in the atmosphere. If these mist globules become larger, they fall to the earth as rain.

95. Relative Humidity and Human Comfort. The water vapor is a very important constituent of the air when considered from the standpoint of human comfort. When the relative humidity is high, human beings become very uncomfortable because the perspiration fails to evaporate promptly from the surface of the body. Now the evaporation of perspiration is one of the most important means of regulating the body temperature, heat being taken up when the moisture evaporates. Hence, when the relative humidity is high, people are usually very uncomfortable. High relative humidity is more oppressive than a high temperature accompanied by a relatively dry atmosphere. The oppressive character of the air in schoolrooms, crowded halls, or other public gathering places is largely due to the high relative humidity caused by the evaporation of perspiration and by the water vapor exhaled with the air from the lungs.

96. Drinking Water. Those who have always lived in cities and have had an abundant supply of clear, pure water whenever they chose to turn the faucet, find it hard to realize what a serious matter the problem of water supply is. Water that is to be used for drinking must be pure from a sanitary standpoint, that is, it must contain nothing that can cause sickness. Bacteria, — microscopic living organisms, — which cause certain diseases, notably typhoid fever, are likely to be present in water as a result of pollution by sewage.

A few bacteria taken into the system in a glass of even badly polluted water are not in themselves harmful, but the danger lies in the fact that they find in the human intestines a favorable place to multiply. So, if a few disease germs get into the system, they may within a short time have increased until there are countless numbers of them. Usually the hu-

man system is strong enough to destroy the disease germs before they gain the ascendancy. But when the system is weakened through abuse, or overwork, or lack of exercise, it falls an easy prey to disease bacteria.

The best safeguard against disease is to keep the body in healthy condition, but still one will not willingly subject it to infection by disease germs. Hence those in charge of city water supplies must be continually on the alert to keep them free from infection. The appearance is not a criterion of the safety of water. The clearest looking water may contain millions of typhoid bacilli, whereas, often, yellow and even muddy water may be quite safe. It requires chemical and bacteriological tests to prove the danger or safety of water, and in city supplies the city chemists and bacteriologists must be depended upon to see to this. In country places, where each house has its own well or spring, the safety of the water should be determined from time to time by analysis. Samples of water are usually tested free of charge at the laboratories of the state board of health. This testing is particularly necessary when the well is near the closet or barnyard, but distance from apparent source of infection cannot always be taken as assurance of safety.

97. The purification of water for sanitary purposes consists in the main in destroying or removing bacteria. Filtration will accomplish the removal if the pores of the filter are small enough. The ordinary filter which screws on the faucet is entirely valueless for this purpose. The type of filter which is made of unglazed porcelain is effective in removing bacteria, but its pores are so small that the water filters very slowly.

Sand filters are used in purifying large city supplies but the safety of these filters is due in part to the action of beneficent

bacteria which abound in the filter and destroy the harmful organisms.

Chemical destruction of bacteria is a great safeguard. When water is stored for a long period in reservoirs, the bacteria are destroyed through the oxidizing action of the air. More rapid destruction may be accomplished through the use of chlorine or bleaching powder, and recently the use of ozone, a particularly active modification of oxygen (see Chapter XV, p. 159) has come into favor, particularly in European cities.

Sterilization by Boiling. In country places which have to depend on polluted wells and in cases of epidemic in cities when the public health authorities cannot control the situation, danger of infection is obviated by boiling the water for at least five minutes, since none of the disease-producing organisms are capable of withstanding the boiling temperature for that length of time.

98. Chemically Pure Water. Water that is pure from a sanitary standpoint may contain considerable quantities of dissolved mineral matter. Indeed, water with a small mineral content is probably more desirable for drinking than absolutely pure water.

Natural waters may be purified of their mineral content by means of distillation (see page 17). Rain water has been subjected to a natural process of distillation and is free from mineral matter except as it drags down smoke and dust from the atmosphere.

99. Water for industrial purposes, as, for example, for use in laundries or for feeding steam boilers, should contain as small a mineral content as possible (see Hard Water, page 201). It is, of course, impossible from the standpoint of expense to distil all the water needed in industrial operations, and it is

therefore very necessary to obtain a natural supply as free as possible from dissolved minerals.

SUMMARY

Water is a colorless, odorless, tasteless, mobile liquid which freezes at 0° C. and boils at 100° C. One volume of liquid water gives about 1700 volumes of steam.

Water is a solvent for a great many substances. Each substance has its own definite limit of solubility. In general solid substances are more soluble the higher the temperature. The solvent power of water makes it very useful for cleansing purposes and essential in the life processes of plants and animals.

Water vapor in the atmosphere is the source of rain and of all natural fresh water. Precipitation occurs when the atmosphere is left more than saturated with water vapor as a result of cooling.

In arid regions, the conveyance of water from a distance permits the raising of abundant crops.

Relative humidity is expressed in per cent of the moisture necessary for saturation at the given temperature.

Human comfort depends largely on the degree of relative humidity.

Drinking water is often rendered dangerous by the presence of disease-producing bacteria, so that wells and other water supplies should be tested.

Impure water may be rendered safe by proper filtration or by sterilization. Water may be sterilized by boiling it for at least five minutes or by the addition of chemical substances such as chlorine or ozone.

Water may be freed of mineral matter by distillation.

Questions

1. How could you make sure that a certain colorless liquid was water?

2. On a cold day, with no tendency for ice to melt, how could you distinguish ice from rock crystal?

3. Cite some experiments by which you can prove that the air of the schoolroom contains water vapor.
4. Why is it necessary, from a chemical standpoint, for us to drink water?
5. Some of our western deserts are very fertile when irrigated. Would they be equally fertile to-day if they had been subjected to rainfall for the past century?
6. Explain the cause of the dew found on the grass in the morning.
7. Why are people so uncomfortable in humid weather?
8. State and explain the necessary precautions to be taken in connection with the source of your drinking water.
9. How are municipal water supplies safeguarded?
10. Why do not the same standards of purity apply to water for drinking and for industrial purposes?
11. Supposing the fresh water supply had given out, how might drinking water be obtained in mid-ocean on a steamship?

CHAPTER X

COMPOSITION OF WATER

IN preceding chapters we have seen that although air was regarded by the ancients as one of the elements, it consists in reality of two different gases, oxygen and nitrogen, not to mention small quantities of several other gases. Water was regarded by the ancients as another of the elements, but we are to show that it is in reality a compound of two elements, oxygen and hydrogen; for it can, by suitable means, be decomposed into these two elements.

100. Decomposition of Water by Hot Iron. For example, by boiling water and leading the steam through a tube containing red-hot iron filings, we find that the vapor which escapes from the farther end of the tube does not entirely condense again to the liquid water, as it would if no chemical change had taken place, but that a part of it remains permanently as a gas, Fig. 18. This gas does not dissolve in water; it is colorless and odorless; it burns readily but it does not itself support combustion; in short, it is an entirely new substance, different in its properties from either the iron or the water used in obtaining it. It is *hydrogen*. This gas cannot have come from the iron, for in all our experience with iron no other substance has ever been obtained from it, that is, iron is an element. The gas must, then, have come from the only other possible source; that is, from the water.

If we examine the substance remaining in the tube, we find, in place of the iron, a black substance which is brittle, rather than malleable like iron. This substance is oxide of iron.

The water, therefore, must have had in it not only hydrogen, but also something which united with the element iron to

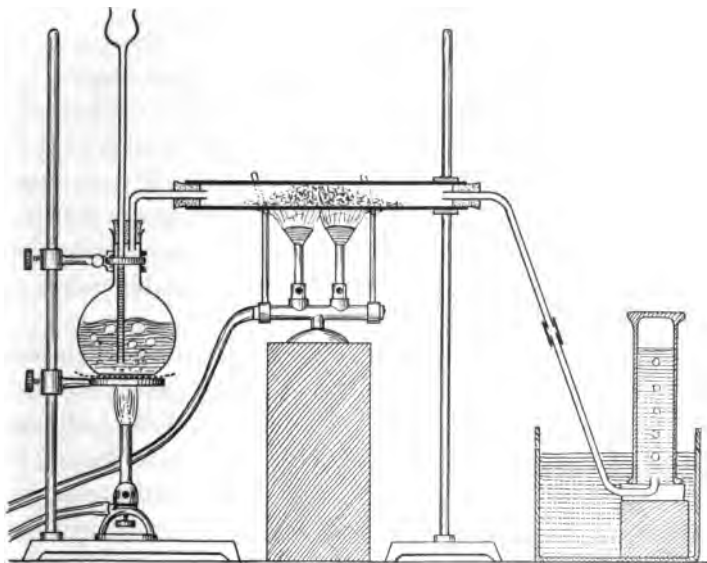


FIG. 18.—Decomposition of Steam by Hot Iron.

form the iron oxide. Upon studying the properties of this iron oxide more completely, we find it to be the same substance that was obtained when iron was burned in pure oxygen (see page 44). As the same elements are required to produce the same chemical substance in every case, we thus have made certain that there must be some oxygen in this new substance formed from iron and water. Since iron is an element, the oxygen must have come from the

water, and water must therefore contain oxygen as well as hydrogen.

101. Decomposition of Water by Sodium. Many other metals when hot can decompose water vapor. Hydrogen is liberated because the metal attaches the oxygen to itself in each case and thus leaves nothing to hold the hydrogen in combination. Some metals are sufficiently active towards water to decompose it even when cold; but such metals are never found free in nature, as they would long ago have been acted upon by natural waters. These very active metals can be prepared by decomposing such of their compounds as are readily available, and this is most often accomplished by the aid of the electric current. One of these metals is sodium, which is prepared in considerable quantities by decomposing sodium hydroxide by means of the electric current.

If a piece of sodium, which is lighter than water, is thrown upon water, a lively action begins at once; a gas is evolved, and the bit of sodium darts round and round the dish, due to the reaction from the pressure of the issuing gas. The sodium melts from the heat evolved by the chemical reaction and then forms a round ball which speedily grows less and less in size and then disappears. If the reaction is carried out under an inverted cylinder full of water, the gas evolved rises to the top of the cylinder.¹ The gas can then be examined and its properties determined. It proves to be hydrogen. Thus sodium can accomplish, in the cold, what iron could only accomplish when the temperature was raised; namely, the displacement of hydrogen from water.

¹ This experiment should be performed only by the instructor, as an explosion may result if not carefully handled.

102. Further Displacement of Hydrogen. If, now, the solution remaining after the action of sodium on water is evaporated to dryness, thus removing all water not acted upon by the sodium, the product is found to be a white solid which has all the properties of the substance known as sodium hydroxide. On powdering this product and mixing it with an equal bulk of powdered zinc and heating the mixture gently in a dry test tube, a quantity of gas is evolved which on testing proves to be hydrogen. Now both sodium and zinc are known to be elements and therefore do not contain hydrogen. The hydrogen, then, since it cannot have come from either of the metals employed, must have come originally from the water. Thus we have twice obtained hydrogen, which was originally a component of the same water, and we can assert that the hydrogen of water exists in two portions, one of which is more easily displaced than the other. An accurate comparison of the amounts of hydrogen set free by the sodium and by the zinc, respectively, has shown that they are equal.

103. Electrolysis of Water; Volume Composition. Our next step in the study of water will be to study the effect of passing an electric current through it. An electric current passes through pure water with great difficulty, but if a little sulphuric acid is added to the water, the current then passes freely. The exact nature of the action of the sulphuric acid in allowing the current to flow more freely will not be explained here, but it may be stated that there is just the same amount of acid present after the passage of a large amount of current as there was at first. In this experiment, then, we shall add a little sulphuric acid to the water as a matter of convenience; but in studying the changes that occur, we shall leave the acid entirely out of account, for as just stated

the acid itself is not permanently altered. The electrolysis of water can best be carried out in an apparatus devised by Hofmann and known as Hofmann's electrolytic apparatus. It consists of three tubes connecting at the bottom, as shown in Fig. 19. Two of the tubes are in the same plane, the

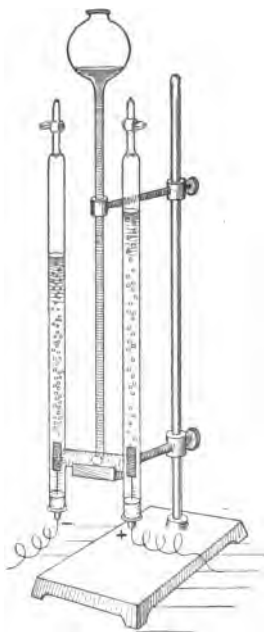


FIG. 19. — Electrolysis of Water.

third is in the rear and is provided with a bulb at the top to act as a reservoir for the acidulated water. In the lower part of the front tubes are placed small pieces of sheet platinum which are supported by platinum wires connected respectively with the two poles of an electric battery. These metal terminals are known as electrodes and it is at the surface of these electrodes that the chemical changes brought about by the electric current take place. The tops of the two front tubes are provided with glass stopcocks through which any gases that collect may be removed for examination.

On filling the apparatus with the acidulated water and allowing the electric current to pass, bubbles of gas at once appear at each of the electrodes and continue to rise so long as the current is passing. It is soon evident that more gas collects at the negative electrode (that is, the one connected with the negative electrical conductor) than at the positive electrode, and when carefully measured under like conditions of temperature and pressure, it is found that the volume of

gas collected at the negative electrode is exactly twice that collected at the positive. On withdrawing some of the gas that occupies the larger volume and testing it, we find that it will burn, but will not support combustion; it is colorless and odorless, and insoluble in water. It has, in fact, the characteristic properties of hydrogen. The other gas, that from around the positive electrode, is colorless and odorless, it will not burn, but it does support combustion; it shows the characteristic properties of oxygen.

104. Synthesis of Water. After showing thus that water can be decomposed into two volumes of hydrogen gas and one volume of oxygen gas, the thought naturally arises: if this is all that water consists of, it should be possible to form water from these two gases when they are taken in the proportion of two volumes of the former to one volume of the latter. And, as a matter of fact, this can be done with perfect ease for there is great chemical attraction between hydrogen and oxygen (it is this attraction for each other that has to be overcome when water is decomposed by the electric current or other means). To form water, it is only necessary to bring hydrogen and oxygen into the presence of each other and to start chemical combination by means of a spark or a small flame. For example, hydrogen gas issuing from a jet may be lighted just as ordinary illuminating gas is lighted. The hydrogen burns, however, with a colorless flame. That water is really a product of this reaction may be proved by holding a piece of cold glass over the flame and noting the moisture that condenses.

105. By means of the apparatus shown in Fig. 20, it can be readily shown that two volumes of hydrogen and one volume of oxygen actually do combine to form water. The inner tube is filled to mark 1 with oxygen and then to

mark 3 with hydrogen, precaution being taken by raising or lowering the apparatus that the top of the mercury column in the tube is always at the same height above the free surface of mercury in the reservoir M. After causing combination to take place by jumping a spark between the terminals of the electrical conductors, E E, we see the mercury almost immediately rise until it reaches the top of the tube, if the experiment is carried out at the ordinary temperature.

When however the experiment is performed while steam is being passed through the outer jacket, thus keeping the temperature constantly at 100°C ., the mercury level rises only to the mark 2 (the same precaution being observed of adjusting the apparatus until the top of the mercury is at the same height above the level in the reservoir).

We have thus shown that at a temperature where water will remain a gas, two volumes of hydrogen combine with one volume of oxygen to produce two volumes of water vapor.

106. Law of Definite Combining Proportions Illustrated. These gases will not combine in any other proportions than those stated. If, for

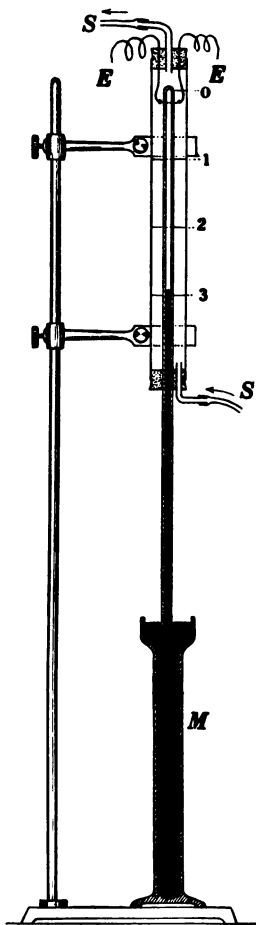


FIG. 20. — Combining Proportions by Volume of Hydrogen and Oxygen.

example, one volume of oxygen is mixed with three volumes of hydrogen, two volumes of the latter combine as before to produce water, while one volume is left uncombined and will remain as a permanent gas even if the tube is cold and the water vapor condenses to liquid water. Similarly, if two volumes of oxygen are mixed with two volumes of hydrogen, it is found, after the explosion, that one volume of oxygen is left uncombined. These facts illustrate again the law of definite proportions.

Such simple and exact relations as are thus observed in the combining volumes of these gases would never exist by mere chance. There must be some underlying explanation for it and we shall try in a forthcoming chapter to develop such an explanation.

107. Weight Composition of Water. Very exact measurements of the weights of these gases have shown that one liter of oxygen at 0° C. and 760 mm. pressure weighs 1.429 g., while one liter of hydrogen weighs 0.08996 g. Since, as we have seen, two volumes of hydrogen combine with one of oxygen, it follows that 1.429 g. of oxygen combine with 0.17992 g. of hydrogen. These weights are in the proportion of 7.94 to 1.00; in other words, 7.94 parts by weight of oxygen combine with one part by weight of hydrogen to produce 8.94 parts by weight of water. The combining weight of oxygen is, then, 7.94, if that of hydrogen is considered as one.

We shall find in every case in which two elements combine, as do hydrogen and oxygen in this case, to form a definite chemical compound such as water, that there is a certain definite ratio between the weights of the two elements that enter the combination. Although these ratios are always absolutely the same for the same combination, they

are not as a rule *simple* whole numbers. Contrasted with this, the ratios of the volumes of gaseous substances which combine are not only absolutely definite, but they are in the proportion of *simple* whole numbers. We shall seek for explanations of these interesting facts in a future chapter.

108. Hydrogen peroxide is a compound that, like water, contains only the elements hydrogen and oxygen, but here we find that 15.88 parts by weight of oxygen instead of 7.94 parts are combined with one part of hydrogen.

The common pharmaceutical preparation which is sometimes sold under the correct name of hydrogen peroxide and sometimes under trade names suggesting the double amount of oxygen, is a mixture of about 3 parts of hydrogen peroxide with 97 parts of water. It is used in cleansing wounds since it has a destructive action on the germs that cause blood poisoning, while it is not injurious to the flesh.

Pure hydrogen peroxide is a sirupy liquid one and one half times as heavy as water. It blisters the skin and will set fire to finely divided cotton. The pure substance is dangerous to handle, since it will explode violently on rather slight provocation. The explosion is due to a sudden decomposition into water and oxygen. In solution in water it is not dangerous, but it decomposes with ease, giving off oxygen and only water remaining. If a pinch of some powdered substance, sand, or, still better, manganese dioxide, is dropped into a 3 per cent hydrogen peroxide solution in a test tube, a vigorous effervescence begins at once and the escaping gas will cause a glowing splinter to burst into flame. The powder can be shown not to have changed chemically, thus it acts only catalytically in hastening the natural decomposition of the hydrogen peroxide.

SUMMARY

Water is not an element as the ancients believed. It is composed of the elements hydrogen and oxygen. It may be decomposed by iron at a high temperature or by a very active metal such as sodium at the ordinary temperature. Hydrogen gas is evolved in these cases and a residue containing oxygen and the metal is left.

Volumetric Composition: Decomposition of water by the electric current and synthesis of water from its elements show that two volumes of hydrogen and one volume of oxygen enter into its composition. When the temperature is high enough to keep the water in the gaseous form, the two volumes of hydrogen and one volume of oxygen yield two volumes of water vapor.

The proportion by weight in which the elements combine in water are 7.94 parts of oxygen and 1.00 part of hydrogen. This relation is as definite but not as simple as the volume relation.

Hydrogen peroxide is another compound of hydrogen and oxygen, and for a given weight of hydrogen it contains exactly twice as much oxygen as does water.

Questions

1. How do you know that the ancients were wrong when they said that water is an element?

2. Which would give a sharper explosion — a mixture of oxygen and hydrogen in which the two gases were present in equal volumes, or one containing two volumes of hydrogen to one of oxygen? Why?

3. Which weighs more — one liter of oxygen or two liters of hydrogen? How much more?

4. Thirty cubic centimeters of hydrogen and 30 c.c. of oxygen are collected over mercury in a measuring tube at 20° C. After exploding the mixture, what will be the volume at 20° C. if the pressure is kept the same?

5. If 30 c.c. of hydrogen and 30 c.c. of oxygen are collected in a measuring tube at 100° C. and the tube is kept at this temperature, by surrounding it with a steam jacket, what will be the total

volume of gases present after exploding the mixture, if the pressure is kept the same? What are the gases? What is the volume of each?

6. An evacuated heavy glass tube is filled at room temperature with oxygen until the pressure is 76 cm. and then hydrogen is forced in until the pressure has risen to 228 cm. The mixture is then exploded by a spark. What will be the condition in the tube after it has cooled to the original temperature?

7. If the same evacuated tube is kept at 100°C. and filled with oxygen to 10 cm. pressure and with hydrogen to 50 cm. pressure, what will be the pressure after the explosion if the temperature is still 100°C. ? — if the tube is cooled to 0°C. ? (Neglect pressure of water vapor at 0°C.)

8. A certain substance yields equal volumes of hydrogen and chlorine gases on decomposition. Find weight per liter of each of these gases in the Appendix (page 428) and calculate the weight composition of the substance.

9. Would a water chemist in "analyzing" a sample of water decompose the water as described in this chapter? Would he be at all interested in a real analysis of water in such a case? Why?

10. In the practical uses of water does the water usually become decomposed?

11. Explain how hydrogen peroxide and water illustrate the law of multiple proportions. What other illustration of this law have we already encountered?

12. Explain the action caused by dropping manganese dioxide into 3 per cent hydrogen peroxide.

13. How does hydrogen peroxide destroy germs?

14. Explain why pure hydrogen peroxide will blister the skin and set fire to cotton.

CHAPTER XI

HYDROGEN

HYDROGEN, as has been seen in the last chapter, is one of the constituents of water, and when liberated from its combination with oxygen in that compound it assumes the form of a gas.

109. Discovery of Hydrogen. Hydrogen was discovered in 1766 by Cavendish, who was the first to make clear its elementary character, but it had been obtained prior to Cavendish's discovery by Paracelsus and perhaps by others while working with active metals and sulphuric acid. It was not called hydrogen by Cavendish, but by Lavoisier who named it from Greek words meaning the water former, because when it is burned in air or oxygen, water is formed.

110. Hydrogen in Water. Water is in fact the most abundant substance of which hydrogen is a constituent. In water, as we have learned in the last chapter, hydrogen and oxygen are held together by some force, so that, instead of having a mixture of two gases, we have the liquid water, a substance which has different properties from either hydrogen or oxygen. By overcoming the force that holds its constituents together it should be possible to separate water again into its elements. As already seen in the last chapter, water can be decomposed into its elements by means of the energy of the electric current; and hydrogen may be set free from water by means of some metals, as

sodium or iron, which possess a greater chemical energy and therefore a greater attraction for the oxygen.

111. Hydrogen from Acids. When hydrogen is to be made in the laboratory, water is not chosen as its source, but rather an acid such as sulphuric acid or hydrochloric acid. An acid always contains hydrogen, although not all substances that contain hydrogen are acids. In an acid the hydrogen is in such a peculiar state of combination that if the acid is dissolved in water and the solution treated with the metal zinc, or iron, or any one of a considerable number of active metals, the hydrogen is displaced by the metal, escaping as a gas, while the metal assumes the place in the acid which was vacated by the hydrogen.

112. Hydrogen Generator. The simplest form of laboratory generator consists of a bottle or flask (Fig. 21) with

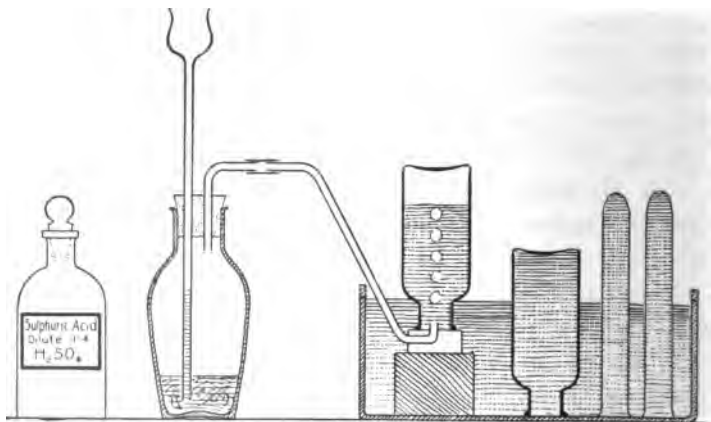


FIG. 21. — Hydrogen Generator.

a two-holed stopper through one hole of which a thistle tube enters, reaching the bottom of the bottle, and thus serving not only for the entrance of fresh acid but also as a

trap to prevent the escape of the hydrogen. The hydrogen passes through a delivery tube which is led through the other hole in the stopper. This tube should just barely pass through the stopper and not be pushed down into the liquid, as there would then be no escape for the hydrogen. The delivery tube leads the gas into a trough or pan of water in which several test tubes or wide-mouth gas bottles have been inverted after having been filled with water. When zinc (preferably in a coarsely granular form, to expose a large surface) has been placed in the generating bottle and covered with water to seal the thistle tube and dilute sulphuric acid is poured in through the tube, a lively effervescence begins. Since the bottle was filled with air at the outset, the gas which first issues from the delivery tube will be a mixture and should be rejected because it is explosive and because it does not have the same properties as pure hydrogen. After a few minutes the air will all have been displaced, and then one of the bottles in the trough may be held over the end of the delivery tube and some hydrogen collected.

113. Properties. Hydrogen burns with a very hot but almost colorless flame. It does not support combustion when a lighted match is thrust into it. It is colorless and odorless when pure (although when prepared as usual from impure materials, other substances may be present in it which have odor of their own).

114. Lightness. Hydrogen is the lightest gas known, one liter of it weighing only 0.09 g., that is, less than $\frac{1}{1000}$ as much as the same volume of water. In virtue of its lightness, it is used to fill balloons, for it is less than one fourteenth as heavy as the air which it displaces. For every liter of hydrogen in the balloon, the lifting power is

equal to the difference in weight between a liter of air and a liter of hydrogen, or, $1.29 - 0.09 = 1.20$ grams.

115. Diffusibility. Hydrogen is the most diffusible of all gases, that is to say, it passes most readily through small openings or through porous material. It is well known

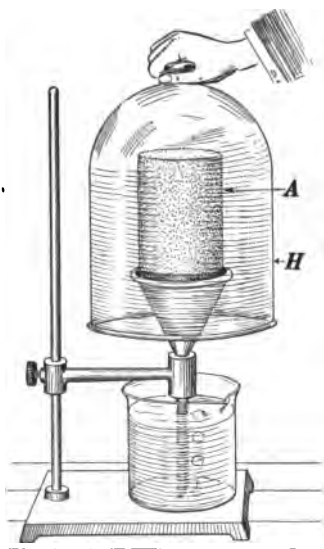


FIG. 22. — Diffusion of Hydrogen
H, bell jar filled with hydrogen.
A, unglazed earthen cylinder
sealed to vertical tube dipping in
beaker of water.

that toy balloons, which are filled usually with illuminating gas containing a considerable amount of hydrogen, soon lose their lifting power. This is very largely due to the diffusion of hydrogen through the rubber skin of the balloon.

The effect of diffusion may be prettily shown if a large jar of hydrogen is placed over an unglazed earthen cylinder filled with air and mounted as shown in Fig. 22. Hydrogen diffusing into the porous cylinder faster than air, which is more sluggish, can diffuse out, a greater pressure is created within the cylinder, and this pressure is conveyed through the tube reaching down and dipping into the beaker of water. Thus bubbles of gas are seen to rise in the beaker almost immediately after the jar of hydrogen is placed over the porous cylinder. If after considerable hydrogen has diffused into the cylinder the jar is removed, the hydrogen inside the porous vessel will diffuse out into the air faster than the air can get in and there will be less pressure inside

than out so that the water in the beaker will be forced by the outside air pressure up into the inner cylinder.

116. Liquefaction and Solidification. Besides being the most diffusible of all gases, hydrogen is, with one exception, the most difficult gas to liquefy and solidify. It has long been known that by great cold and pressure air could be condensed to a liquid, although it is only comparatively recently that the liquefaction of air on a commercial scale has been possible. But it was not until 1898 that hydrogen was first liquefied. Dewar, an English scientist, accomplished this. Under ordinary atmospheric pressure it liquefies at about -252° C., or only 21° above the absolute zero. If it is highly compressed, the gas liquefies more easily, that is to say, at a higher temperature, but above the temperature of -241° C. or 32° absolute, which is known as its *critical temperature*, it cannot be liquefied at all. It is thus evident why, for so long a time, hydrogen resisted all efforts to bring it into the liquid form. Pressure alone was not sufficient; a very low temperature was necessary, and many attempts were made before this was finally attained. Liquid hydrogen freezes at -257° C. or 16° absolute.

Both the liquid and the solid are colorless.

117. Detonating Gas. A mixture of two volumes of hydrogen and one volume of oxygen (the ratio by volume in which they combine to form water) is known as detonating gas because it detonates or explodes so violently when ignited by a spark or kindled in any other way. If soap bubbles are blown with this mixture and lighted as they float away, they explode with a deafening report. This explosion is due to the great heat liberated when the hydrogen combines with oxygen. This heat expands the resulting gaseous product (steam) so suddenly and to such an extent

that a violent blow is struck against the surrounding air, thus producing the loud noise. Mixtures of hydrogen and oxygen in other proportions than 2 to 1 are also more or less explosive, as are also mixtures of hydrogen with air. Mixtures of illuminating gas (which usually contain considerable hydrogen) with air are similarly explosive, hence the need for great caution in regard to using an open flame in the vicinity of a gas leak.

118. Oxyhydrogen Flame. The great heat of combustion of hydrogen is utilized for obtaining very high temperatures by means of the oxyhydrogen blowpipe, a device in which hydrogen and oxygen are led into a small mixing chamber from which they issue into the flame (Fig. 23).

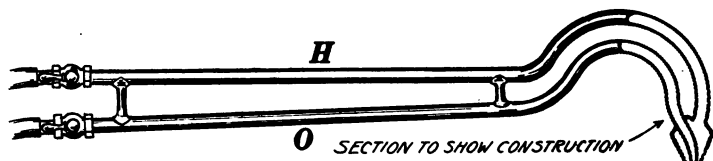


FIG. 23. — Oxyhydrogen Blowpipe.

The operation of the blowpipe is as follows: first the hydrogen cock is opened and the gas is lighted and burns with the oxygen of the air. Then the oxygen cock is gradually opened, introducing oxygen into the interior of the flame. The flame grows sharp and pointed and the inside blue cone retreats more and more with increasing supply of oxygen until it is very short and barely reaches beyond the orifice. The two gases are then issuing in the correct combining proportions and the most intense heat can be obtained for they are already mixed and ready to combine as they leave the orifice. It frequently happens, if the flame is not skillfully manipulated, that it strikes back into the mixing chamber

and produces a sharp report from the explosion *théré*. The mixing chamber is made so small, however, that if the flame accidentally strikes back, it will not produce a troublesome explosion.

119. With the oxyhydrogen flame, a temperature of about 2500° C. can be obtained, which is sufficient to melt such ordinarily infusible substances as platinum, quartz, and aluminium oxide. The limit to the temperature which can be obtained is set by the point at which water vapor itself will decompose, for when water vapor is heated to 2500° C. a large part of it is decomposed into hydrogen and oxygen gases, by which process it absorbs heat instead of evolving it. In just the same way, mercuric oxide is decomposed by heat into mercury and oxygen, only this occurs at a much lower temperature.

120. There are many practical applications of the oxyhydrogen flame in cases where a very high temperature is needed. One of the most interesting of these is in melting aluminium oxide in making artificial rubies and sapphires. These stones are composed of aluminium oxide with slight admixtures of other oxides. Aluminium oxide can only be melted at temperatures above 2000° C. It is a common enough substance and in its ordinary form is of very small value; but by melting it in the oxyhydrogen flame, clear, transparent, finely colored stones can be made that are equal in beauty to the natural gems.

121. With air hydrogen gives a very hot flame, but not so hot as with pure oxygen, because four volumes of cold nitrogen are mixed with every volume of oxygen that enters the flame, and a considerable part of the heat of combustion must be used to bring this nitrogen up to the temperature of the flame.

122. Hydrogen Burns in Chlorine. Not only does hydrogen combine with oxygen but also with other elements, notably chlorine, which is to be studied a little later. If a jet of burning hydrogen is inserted into a jar of chlorine gas, it continues to burn, but now combines with the chlorine instead of with oxygen, forming hydrogen chloride instead of hydrogen oxide (water). By making a mixture of one volume of hydrogen and one volume of chlorine, an explosive mixture is obtained which resembles in its violence the oxygen-hydrogen mixture.

123. Reducing Action. On account of its great affinity for oxygen and for chlorine, hydrogen can, in many cases, take these elements away from the metallic elements with which they are frequently combined, thus leaving the metallic element uncombined. Thus if black copper oxide is placed in a glass tube through which hydrogen is being passed and if the tube is heated, the black oxide of copper changes, and in its place we see red metallic copper while at the same time drops of water condense in the cooler part of the tube, showing that the oxygen of the oxide united with the hydrogen to form water. This type of chemical action in which oxygen, or an element similar to oxygen, is taken away from its combination with a metal is called *reduction*. The copper oxide is *reduced* to the metallic condition by the heated hydrogen.

124. Gaseous Fuels. The great heat of combustion of hydrogen makes it valuable for fuel purposes. It is, however, too costly in the pure state to use for any except very special purposes where comparatively small quantities are needed.

Many kinds of artificial gas such as those used for illuminating purposes contain large amounts of hydrogen either

in the free state or combined with carbon or both free and combined. These mixtures make splendid fuel, as they give great heat without making smoke or leaving ashes, the products of combustion being invisible gases.

Whenever it can be obtained, illuminating gas is used rather than pure hydrogen for filling balloons, as, being in most cases about one half hydrogen, it is fairly light and is much cheaper.

SUMMARY

In decomposing water, energy is required to overcome the attraction between oxygen and hydrogen. This energy is supplied by the electric current or by the greater chemical energy of some metal such as sodium, which is more active than hydrogen.

Hydrogen may be more easily obtained from acids than from water. Any active metal such as zinc will displace the hydrogen of an acid.

Properties of Hydrogen: Hydrogen is the lightest and most diffusible gas known. It is with one exception the most difficult gas to liquefy. Free hydrogen has a strong tendency to combine with oxygen, and the heat produced by the combination gives the very high temperature of the oxyhydrogen flame.

Hydrogen is a reducing agent, since it can withdraw oxygen from its combination with many of the metals in their oxides. Hydrogen forms compounds also with other non-metals than oxygen, notably with chlorine.

Questions

1. What chemical property of hydrogen was responsible for its name?

2. What has to be overcome to separate the hydrogen from the oxygen in water? Mention two different methods for accomplishing this.

3. How is it that sodium can decompose water when there is so strong a force holding the hydrogen and the oxygen together?

4. From what source is hydrogen released more readily than from water?

5. How could you distinguish hydrogen from other colorless, odorless gases, such as oxygen, or nitrogen?

6. What property of hydrogen accounts for the constant loss of gas from a hydrogen balloon?

7. Why is the flame of hydrogen burning in the air less hot than that obtained when hydrogen burns in oxygen?

8. What practical use is made of impure hydrogen?

9. Why is illuminating gas so much used for filling balloons?

10. Why do not gas stoves create a smoke nuisance?

11. Under what conditions does a gas flame smoke? Explain why.

12. How might metallic iron be obtained from ordinary iron rust?

13. Some clean, dry iron filings which weigh 5.1300 g. are heated in a current of steam and afterward are found to have increased in weight to 5.8446 g. What weight of hydrogen has been liberated and what volume would it occupy under standard conditions?

14. Eleven and two tenths liters of hydrogen measured under standard conditions are passed through a heated tube containing dry copper oxide. What weight of water could be condensed beyond the heated tube?

CHAPTER XII

THE ATOMIC THEORY

WE have learned that when chemical substances combine to form definite new substances, they do so in perfectly definite proportions. For example, in a case already dwelt upon at some length, one part by weight of hydrogen combines with 7.94 parts by weight of oxygen, no more, no less, to form 8.94 parts of water. Almost countless illustrations of similar definite combining proportions might be cited.

This definiteness of the combining proportions is a very important characteristic of chemical compounds, and it is one that is often used to distinguish compounds from physical mixtures. Thus, as we have seen, one of the reasons why we believe air to be merely a mixture of oxygen and nitrogen is that it can contain these two elements in varying proportions.

125. Law of Definite Proportions. It is repeatedly found in the study of nature that a certain striking regularity exists among a great number of otherwise more or less different phenomena. When this regularity is reduced to words, and the statement so made is found always to be true, this statement becomes known as a *law*. The law of definite proportions would read thus: *Whenever two or more elements are combined with each other in a definite chemical compound, the weights of the elements in that compound are to each other always in the same definite numerical ratio.*

126. Hypothesis and Theory. When such a law exists, it cannot be accidental; there must be some underlying cause for it. Scientific men are impelled to speculate upon the nature of things beyond what can actually be seen and felt, and thus, if possible, to reach a better understanding of the workings of nature. Any suggestion as to the underlying causes of natural phenomena is known as an *hypothesis*. When an hypothesis has been found to fit a large number of cases, and thus to be of very general importance, it becomes known as a *theory*.

127. Atomic Theory of Dalton. In an attempt to explain the nature of matter, the *atomic hypothesis* in a crude form was brought forward by the very ancient philosophers, prominent among whom was Democritus (about 400 B.C.). When, with the increase in the knowledge of chemical facts, the law of definite proportions became recognized (late in the eighteenth century), it was found that the atomic hypothesis furnished for this law a beautiful explanation. The law of multiple proportions, which was discovered a little later, could likewise be explained by the atomic hypothesis. Thus this hypothesis rose to the dignity of a theory and is known as the Atomic Theory. This theory is closely associated with the name of Dalton, and is often spoken of as Dalton's atomic theory because it was Dalton who was the first to clearly see the application of the hypothesis to the laws of definite and multiple proportions.

As has already been said, a crude form of the atomic hypothesis was advanced many centuries ago by the old Greek philosophers. They observed that any body of matter could be divided into pieces, each piece could be divided into smaller pieces, each of these smaller pieces could be divided, and so on until the pieces were smaller than could

be distinguished with the eye. They could not see any limit to the divisibility, and yet they could not conceive of the subdivision going on without limit. They therefore imagined the existence of atoms, very small indivisible particles of which all matter was composed.¹ Bodies of matter were simply aggregates of atoms, and the aggregates could be divided until the single atoms were reached, but no further.

When at a much later day it became recognized that there were a number of entirely distinct elements of which the earth was composed, the idea of atoms became more specific, for it was thought that the atoms of any one element must all be alike but that the atoms of different elements must be different.

The final form was given to the atomic theory by Dalton, who made it plain, that, when elements unite to form a compound, it must really be the atoms which unite in pairs or in simple groups. They must therefore be regarded as having some sort of attraction for each other. Dalton especially emphasized, as a vital part of his theory, that all the atoms of a given element are exactly alike in *weight* as well as in all of their other properties, but that atoms of different elements differ in weight and in many of their other properties.

128. Analogy of Atomic Theory. Red beans and green peas could be put into the same pail and shaken together and a mixture thus obtained that would have a mottled appearance, some of the small bodies being red and others green. There might be more beans or there might be more peas without essentially changing the mottled appearance of the mixture. Now let us suppose a case that would be analogous to a case of chemical combination.

¹ The word *atom* comes from the Greek, and means indivisible.

Suppose that each bean had a latent power to attach to itself just one pea, — no more and no less. Suppose, further, that this power was very strong and that at a given signal it might be brought into operation. When the signal was given, the mixture of beans and peas would be thrown into violent agitation, — the individual particles would be pulled to and fro in the effort to attach themselves to their partners. Finally the mass would come to rest again, and if at the outset there had been exactly the same number of peas as beans, we should have now only pairs composed of one bean and one pea each, and no unattached beans or peas would be left. If at the start there had been more beans than peas, there would now be some single beans left unattached; if at the start there had been more peas, there would now be single peas.

The foregoing is a fair analogy to what is supposed to take place, according to Dalton's atomic theory, when two elements, for example hydrogen and oxygen, unite. These two gases may be mixed in any proportion whatever so long as no signal is given for them to enter into chemical combination. Only a mixture is produced like that of the beans and peas. This mixture appears uniform because we are incapable of distinguishing particles so small as the atoms, but if our vision were more powerful, there would doubtless be some such mottled appearance as that of the beans and peas. Now when the signal for the two elements to combine is given, for example when an electric spark is passed through the mixture, the agitation caused is so violent that we see the effect of an explosion. After the explosion there is an entirely different substance, as we know; its smallest particles cannot be atoms, because they contain both hydrogen and oxygen. The smallest particles of the compound are called *molecules*.

We learned in Chapter X that water contains two parts of hydrogen because one part can be set free before and more easily than the other. Perhaps, then, in the molecule of water there are two atoms of hydrogen to one atom of oxygen. If we consider the red bean to represent the oxygen atom and the pea the hydrogen atom, our new molecule may be pictured as consisting of a bean with two peas instead of one attached to it.

129. Analogy Applies to Multiple Proportions. In our analogy with beans and peas let us make a still further supposition. After every bean has found one pea to which to attach itself, suppose that it still has some attractive power for a second pea, although considerably less than for the first. If there were enough more peas in the mixture, each bean might acquire two peas and a new kind of grouping would be in evidence in which one bean would be attached to two peas. The fact that almost the exact counterpart of this analogy is frequently met in chemistry furnishes us our strongest reason for believing in the essential truth of the atomic theory.

The law of multiple proportions is illustrated by the two oxides of carbon which were discussed in Chapter VI. **The Law of Multiple Proportions** may be stated as follows:

When two elements are able to form more than one definite compound, if such weights of each of the compounds are taken that they contain the same weight of the first element, then the weights of the second element in the different compounds are to each other in the ratio of small whole numbers.

To return to our analogy, let us consider the two different kinds of groups of beans and peas. In each group we had one bean, but in the second group we had two peas instead of one as in the first group. The number of peas in the two

groups are in the ratio of small whole numbers, namely as one is to two. In carbon monoxide let us suppose that the smallest particle of the compound, that is, the molecule, contains just one atom of carbon and one atom of oxygen. Then for carbon dioxide, which we know contains twice as much oxygen to a given amount of carbon, we should have two atoms of oxygen combined with each atom of carbon.



FIG. 24. — A Conception of the Structure of Molecules.

We can imagine the molecule as looking somewhat as the arrangement of beans and peas. In the

diagram (Fig. 24) each white sphere is meant to represent an atom of oxygen and each black sphere an atom of carbon.

130. Value of Atomic Theory. If no one had ever conceived of the atomic theory, it seems as if it would be impossible for us to give any plausible explanation of the remarkable fact that elements combine in definite and in multiple proportions. It must never be lost sight of, however, that the atomic theory is only an attempt at an explanation. We cannot see the atoms, and we shall probably never be able to verify by direct observation the correctness of the atomic theory. The value of the atomic theory is that it does explain satisfactorily the facts regarding chemical combination, and thus explaining, it serves as a framework for building the structure of our knowledge of chemical facts.

It may be stated that there is a great deal more evidence in support of the atomic theory than that given here. To understand this evidence requires a knowledge of mathematics and of physical science; nevertheless the atomic theory has been so strengthened thereby that we can as

nearly accept the existence of atoms for an absolute certainty as anything which it is impossible to see by direct observation.

131. Possible Complexity of Atoms. It was formerly supposed that the atoms were very small, hard, elastic spheres which were absolutely indivisible. Recent discoveries have tended to show that the atoms are really very complex, but if this is true, it nevertheless remains a fact that we are unable by any agency under human control to break apart the atoms into smaller particles or to build up atoms from smaller particles. So far as the chemist is concerned the *idea of atoms as indivisible particles may be taken without reservation.*

132. Molecules. It is practically a certainty that matter consists of atoms and that there are as many different kinds as there are elements (*i.e.* about eighty), and that the atoms of any given element are all exactly alike in weight and in all of their properties. When elements combine to form compounds, it is then really the atoms which unite to form atom groups and these groups are the smallest particles, that is, the molecules of the compounds.

So far we have not shown any way in which to tell how many of the atoms of each element enter into the formation of the molecule. We have, however, spoken of the wonderful simplicity shown in the combining volumes of gases, and in a later chapter we shall show that much light is thrown upon this problem by a study of these combining volumes.

SUMMARY

Law of Definite Proportions. When two or more elements are combined with each other in a definite chemical compound, the weights of the elements in that compound are to each other, always, in the same definite numerical ratio.

Law of Multiple Proportions. When two elements are able to form more than one definite compound, if such weights of each of the compounds are taken that they contain exactly the same amount by weight of the first element, then the weights of the second element in the different compounds are to each other in the ratio of simple whole numbers.

A natural law is a statement of a general truth which is capable of being proved by direct observation.

An hypothesis is a suggestion advanced to explain any truth of nature.

A theory is an hypothesis which has been thoroughly tested and found to explain a great number of facts. A theory cannot become a law because it is incapable of proof by direct observation.

According to the atomic theory, matter is made up of infinitely small particles called atoms. The atoms of each of the elements are alike, but different from those of the other elements. It is the atoms themselves which are concerned in the formation of chemical compounds, for different atoms attract and hold each other in small definite groups which are called molecules and which are the smallest possible particles of the compound. Thus the atomic theory explains the law of definite proportions and the law of multiple proportions. Although the atomic theory can hardly be proved by direct observation, it is abundantly proved by deduction. It is of the greatest service in chemistry, for it furnishes a framework for building the structure of our knowledge of chemical fact.

Questions

1. On what two groups of facts was Dalton's atomic theory based?
2. How does an hypothesis differ from a theory?
3. Was the idea of an atomic structure of matter original with Dalton?
4. Use the atomic theory to explain what happens when charcoal burns.
5. Discuss water and hydrogen peroxide from the viewpoint of the atomic theory.
6. Of what use is the atomic theory?

CHAPTER XIII

HYDROGEN CHLORIDE

A METHOD of preparing hydrogen chloride was touched upon in the chapter on hydrogen when the ability of hydrogen to burn in chlorine was described. Hydrogen chloride is to demand our attention in the present chapter.

133. Formation and Recognition of Hydrogen Chloride. For its study in the laboratory, hydrogen chloride can be prepared more easily by another method than the one already mentioned. If a pinch of sodium chloride, that is common salt, is placed in a test tube and covered with a few drops of concentrated sulphuric acid, and perhaps warmed a little, a colorless gas is evolved which has a sharp and very choking odor. On blowing the breath across the mouth of the tube, a white cloud is formed; and on bringing near the mouth of the tube a piece of filter paper wet with ammonia water, a very dense white smoke appears. These properties are very characteristic of hydrogen chloride gas and serve admirably as a means of recognizing it.

134. Hydrogen Chloride Generator. When larger quantities of hydrogen chloride are to be prepared in the laboratory, a somewhat more elaborate apparatus than the simple test tube must be used. Some coarse rock salt is placed in the bottom of a large flask, provided with a two-holed rubber stopper. Through one hole passes a thistle tube which reaches to the bottom of the flask; through the other hole

passes a short elbow tube for leading away the gas (see Fig. 25). To start the evolution of gas, concentrated sulphuric acid is poured through the thistle tube until it stands high enough in the flask to seal the lower end of the tube. In order to maintain a vigorous evolution of gas, the flask is

warmed rather cautiously with a Bunsen flame, when it becomes necessary.

Hydrogen chloride cannot be collected over water because of its great solubility. Dry collecting bottles are therefore set upright and the gas is led downward through the delivery tube to the bottom of the bottle. The hydrogen chloride is heavier than air, and as it rises and fills the bottle it lifts the air and forces it out. Of course the hydro-

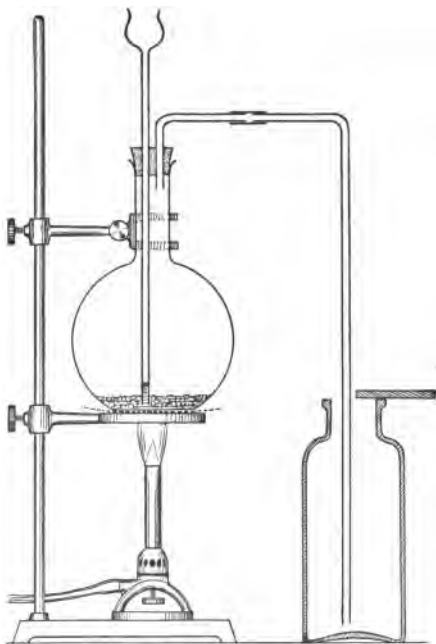


FIG. 25. — Hydrogen Chloride Generator.

gen chloride mixes quite rapidly with the air by diffusion; still if the gas is supplied rapidly and the top of the bottle loosely covered with a glass plate, the gas can be collected nearly pure.

135. Great Solubility. An interesting experiment showing the great solubility of hydrogen chloride is to close the

neck of a large bottle of the dry gas with a one-holed rubber stopper through which passes a short straight glass tube (Fig. 26). Now, on inverting the bottle and thrusting its neck into water, a fountain soon begins to play from the narrow end of the glass tube and this continues until the bottle is practically full of water. Hydrogen chloride is so very soluble that as soon as a little water enters the bottle a nearly complete vacuum is created. The pressure of the air outside is now no longer counter-balanced by the pressure of a gas inside the bottle, and water is forced with some violence through the nozzle of the tube.

Hydrogen chloride is one of the most soluble of gases; one cubic centimeter of water at ordinary

temperature will dissolve 450 cubic centimeters of the gas. This amount of gas weighs 0.8 gram, and thus one gram of water will dissolve 0.8 gram of hydrogen chloride to form 1.8 grams of solution.

The volume of this solution is 1.5 cubic centimeters and thus the dissolving of the 450 cubic centimeters of the gas in 1 cubic centimeter of water increases the volume of the latter by only one half of a cubic centimeter.

It was stated in a preceding paragraph that hydrogen

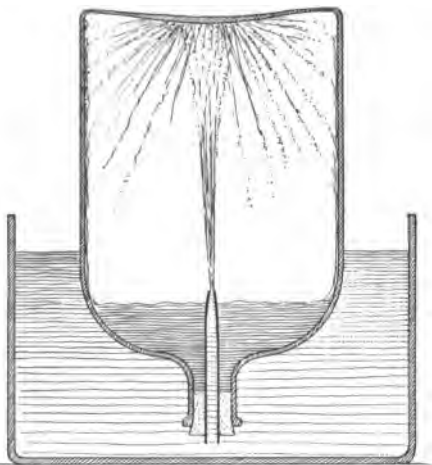


FIG. 26. — Fountain Experiment showing Great Solubility of Hydrogen Chloride.

chloride was a colorless gas, and yet it was also stated that a white cloud is seen when the breath is blown across the mouth of a test tube from which the gas is issuing. The white cloud, however, does not consist alone of hydrogen chloride, and furthermore, it is not a gas at all but it consists of a vast number of little liquid droplets which are condensed from the moisture in the breath together with the hydrogen chloride. These droplets consist, then, of a solution of hydrogen chloride, and their formation results from the great solubility of the gas.

It is still strictly true that hydrogen chloride gas is colorless and invisible. It only becomes visible as a result of condensation with moisture, but such condensation usually occurs when the gas escapes into the air, for the air always contains some water vapor. Thus a little cloud is almost always seen above the mouth of the bottle of concentrated hydrochloric acid when the stopper is removed.

136. Hydrochloric Acid. Hydrogen chloride, when dissolved in water, is most commonly known as muriatic acid or as *hydrochloric acid*, for when in solution it possesses the properties of a strong acid. In the form of the dry gas, it possesses no acid properties. Muriatic acid is the commercial term, while hydrochloric acid is the scientific name for the solution.

It is already known from the chapter on hydrogen that acids contain hydrogen which can be driven out by zinc and some other metals. Two other very characteristic properties of acids are their sour taste and their ability to change the color of litmus from blue to red. Litmus is a vegetable dyestuff which is very sensitive to acids and alkalies, it being turned red by acids and blue by alkalies. Usually strips of paper are colored with the dye, and a strip of paper thus

colored blue will immediately change to red when dipped in acid.

When hydrochloric acid is treated with pieces of zinc, a vigorous evolution of hydrogen takes place. Hydrochloric acid turns blue litmus to red and it tastes excessively sour. In fact, concentrated hydrochloric acid is very corrosive and totally unsafe to taste; one part of this acid diluted with one hundred parts of water gives a solution which will change litmus to red and which is sour although quite safe to taste.

137. Method of Manufacture. From a practical point of view, the dry hydrogen chloride is of little importance, but in solution as hydrochloric acid it finds extended use. The method of its manufacture on a large scale is not different in principle from that of the laboratory preparation. Common salt is treated in large cast-iron pans with concentrated sulphuric acid. The pans are heated by a fire built underneath. When the reaction is one half completed, the charge in the pans is raked upon hearths of fire brick where it is heated much hotter and the reaction is carried to an end. The gas is led off through flues and brought in contact with water so that it is entirely dissolved. The saturated solution that is thus obtained contains about 40 per cent by weight of hydrogen chloride and is known as concentrated hydrochloric acid.

138. Uses of Hydrochloric Acid. Considerable quantities of hydrochloric acid are manufactured for use in the industrial arts. Most of this is sold in the somewhat impure condition known as muriatic acid. Some, however, is further purified and sold as C.P. (meaning chemically pure) hydrochloric acid. The acid is usually shipped in large glass carboys packed in wooden boxes with some sort of packing material to prevent breakage. Such carboys are to be seen

at many manufacturing plants. The acid is used by tinmen and plumbers for cleaning metal surfaces to be soldered. Hydrochloric acid is also used in preparing chlorides of the metals, in preparing chlorine and hydrogen in the laboratory, in making aqua regia, and in analytical work both in schools and colleges and in practical analytical laboratories. The use of this acid is not nearly so extensive as that of sulphuric acid, which is much cheaper and serves equally well many of the purposes for which an acid is required. Likewise when a compound containing chlorine is required, it is customary to use sodium chloride on account of its cheapness, rather than the more expensive hydrochloric acid.

139. Nature of the Reaction in the Generator. Concentrated sulphuric acid is composed of hydrogen, sulphur, and oxygen. It may be called hydrogen sulphate, as we shall see later, just as hydrochloric acid is called hydrogen chloride. Sodium chloride, as the name implies, is a compound of sodium and chlorine. When sulphuric acid and sodium chloride interact, the hydrogen of the former and the chlorine of the latter combine to form hydrogen chloride, which in virtue of the fact that it is a gas, escapes readily from the mixture and is thus obtained in the pure condition. The sodium of the sodium chloride and the sulphur and oxygen of the sulphuric acid are still to be accounted for. They combine to form another new substance, sodium sulphate. The residue left in the generator after the evolution of hydrogen chloride according to the laboratory process, is a solid substance. As ordinarily left, it will doubtless contain either some unused sodium chloride or sulphuric acid, but by a process of purification, pure sodium sulphate can be separated from it. This substance is another salt and has many similarities to common salt in its appearance and in other of its properties.

140. Composition. We already know from the first-mentioned method of formation in which hydrogen is burned in chlorine, that hydrogen chloride is composed of hydrogen and chlorine and solely of these two elements. The scientific men of earlier days who helped to bring our science of chemistry to its present standing, did not possess as much knowledge as we. They discovered the substance we call hydrogen chloride by treating salt with sulphuric acid, and they called it muriatic acid, — meaning the acid obtained from sea salt. It was found that zinc acting on the acid solution set free hydrogen. It was believed that zinc was an element and did not contain hydrogen; and it was known that zinc acting on water alone did not liberate hydrogen. Hence it was believed that the hydrogen came from the muriatic acid. What was apparently another constituent of the muriatic acid was obtained by treating it with a black substance which we know as manganese dioxide. A greenish-yellow, ill-smelling gas was obtained which was called chlorine on account of its color (*chloros*, meaning green). Manganese dioxide was known to give off oxygen when strongly heated. Now possibly on reacting with muriatic acid, the manganese dioxide gave up some oxygen to combine with the hydrogen of the acid and form water, thus leaving the residue of the muriatic acid uncombined and free to escape as the evil-smelling, greenish-yellow gas, chlorine.

The next step in establishing the composition of muriatic acid was to see if it could be made from hydrogen and chlorine. This was, of course, found to be possible, and when, with further study, it was decided that chlorine as well as hydrogen was an element, the chemical nature of muriatic acid was definitely settled.

141. Combining Ratio by Volume. When concentrated hydrochloric acid is electrolyzed, it is found that hydrogen is evolved at the negative electrode and chlorine at the positive. When water was electrolyzed, we found that two volumes of hydrogen and one volume of oxygen were obtained. We

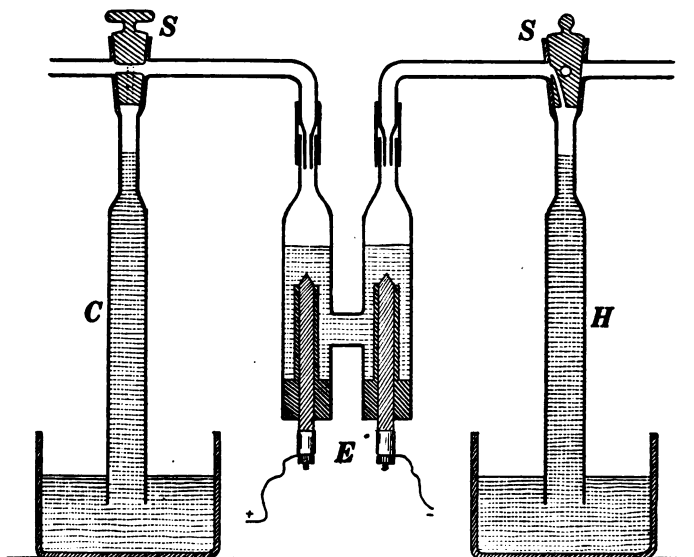


FIG. 27. — **Electrolysis of Hydrochloric Acid.** *E*: electrolytic cell; *SS*: three-way stopcocks which may be turned so that the gases run to waste until solution in cell *E* has become saturated with chlorine; when the gases are being evolved at a uniform rate, the stopcocks are turned and the gases collected in the measuring tubes *C* and *H*. These tubes are filled with a saturated salt solution which dissolves but little chlorine.

find in the case of hydrochloric acid that we obtain equal volumes of hydrogen and chlorine. In order to show this fact satisfactorily, the experiment must be performed in a specially designed apparatus such as that shown in Fig. 27. Chlorine is somewhat soluble in water and slightly so in hydrochloric acid, and if the experiment is carried out in the

ordinary Hofmann electrolysis apparatus (see page 104), so much chlorine is dissolved that a true measure of its volume is not obtained.

Although we obtain equal volumes of hydrogen and chlorine from the hydrochloric acid, we cannot be absolutely sure that these gases have come from the hydrogen chloride and not from the water. If we could now show that equal volumes of hydrogen and chlorine combine with each other,

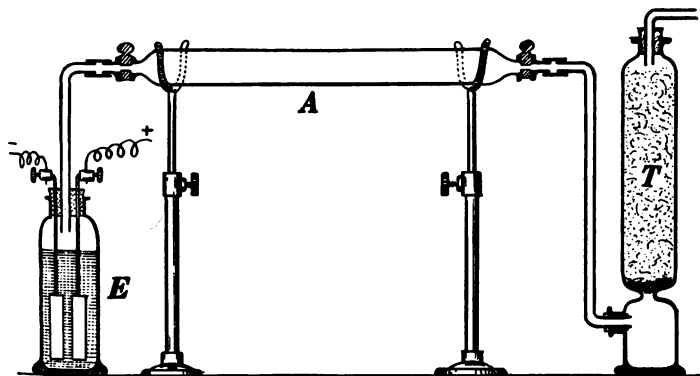


FIG. 28. — Collecting Electrolytic Hydrogen and Chlorine. *E*: electrolytic cell; *A*: explosion tube; *T*: tower packed with lime and glass wool to absorb waste chlorine.

our proof would be complete. To this end we can obtain a mixture of equal volumes of hydrogen and chlorine and then we pass the mixture through a delivery tube into the explosion tube shown in Fig. 28. When all the air is driven out and the tube is filled with the mixture at atmospheric pressure, the stopcocks at both ends are closed. The explosion of this mixture can be brought about even more easily than that of the oxygen-hydrogen mixture. Exposure to direct sunlight or to a magnesium flashlight such as is used in photography is all that is necessary. Of course the

explosion tube should be strong, and furthermore a shield should always be kept between the tube and the observer.

If, as we suspect, the gases combine in the ratio of one to one by volume, there should now be no gas in the tube except hydrogen chloride. To find the volume of the product, one end of the tube may be placed under concentrated sulphuric acid (in which hydrogen chloride is not soluble) and the stopcock opened. We find that the liquid does not rise in the tube nor do bubbles escape through the acid. Hence the volume of the hydrogen chloride at atmospheric pressure is just equal to the sum of the volumes of the hydrogen and chlorine. To finally prove that the gaseous product is hydrogen chloride, we dip the end of the tube into water and find that the water rises until the entire tube is filled.

These experiments prove that *one volume of hydrogen combines with one volume of chlorine to form two volumes of hydrogen chloride gas.*

It was found (p. 103) that hydrogen is combined in two different portions in water, for one portion can be displaced by sodium; and from sodium hydroxide, the new substance formed, still another portion of hydrogen can be obtained by treating this product with zinc.

In hydrogen chloride, on the other hand, hydrogen is combined all in the same portion, so far as we can tell, for if sodium reacts with hydrogen chloride, sodium chloride is formed and hydrogen is liberated, but the sodium chloride is incapable of giving off any more hydrogen.

142. Hydrogen Chloride and the Atomic Theory. Viewed in the light of the atomic theory, it is obvious that every molecule of hydrogen chloride must contain hydrogen and chlorine atoms. The simplest arrangement that we can imagine for the molecule of the compound is that it contains

only two atoms, one of hydrogen and one of chlorine. All the facts that we have so far described are in accord with this view, and unless further facts are brought forward to combat it, we shall adhere to this view and write the formula of hydrogen chloride as HCl .

The combining ratio by weight of hydrogen chloride is 1 part of hydrogen to 35.2 parts of chlorine. As with hydrogen and oxygen, the ratio by weight is perfectly definite, although not in simple whole numbers as the volume ratio. If it is true that hydrogen and chlorine combine atom for atom, it follows that the atom of chlorine weighs 35.2 times as much as the atom of hydrogen.

SUMMARY

Hydrogen chloride is prepared by the action of concentrated sulphuric acid on sodium chloride.

Properties of Hydrogen Chloride. Hydrogen chloride is a colorless gas with an extremely irritating odor. It forms a cloud with moist air and a dense white smoke with ammonia. It is extremely soluble in water and is heavier than air.

In solution in water it is a strong acid and is called muriatic or hydrochloric acid; in this solution it shows the characteristics of acids in that it reacts with zinc, evolving hydrogen; it tastes sour and it colors blue litmus red.

Composition of Hydrogen Chloride. Hydrogen chloride contains only hydrogen and chlorine. One volume of hydrogen will combine with one volume of chlorine to yield two volumes of hydrogen chloride.

By weight, hydrogen chloride contains 35.2 parts of chlorine to one part of hydrogen. The weight relation is definite, although not so simple as the volume relation.

It seems probable that hydrogen and chlorine combine in the ratio of atom for atom. The atom of chlorine weighs, then, 35.2 times as much as the atom of hydrogen and the formula of the compound may be written HCl .

Questions

1. How is hydrochloric acid made?
2. What elements does hydrogen chloride contain and how may it be shown by experiment?
3. What is the volume relation of the constituents of hydrogen chloride? By what experiments can it be shown?
4. What are the properties of dry hydrogen chloride?
5. How do the properties of hydrochloric acid in solution differ from those of the dry gas?
6. What are the uses of hydrochloric acid?
7. Chlorine is allowed to enter a 100 c.c. evacuated tube until the pressure rises to 20 cm.; then hydrogen is admitted until the total pressure is 76 cm. After exploding the gas mixture what will be the total pressure of the gases when they have returned to the initial temperature?
8. If one end of the tube from above question is opened under water and the water allowed to rise as far as it will, what volume of gas at 76 cm. pressure will be left?
9. How does muriatic acid serve a useful purpose in soldering metals?
10. Why is less hydrochloric than sulphuric acid used in the arts?

CHAPTER XIV

AVOGADRO'S THEORY

WE have seen in the chapter on the atomic theory that all matter is composed of atoms of which there are as many different kinds as there are different elements. Since compounds contain more than one element, their smallest particles must contain more than a single atom. The smallest possible particles of a compound are called *molecules*.

The atomic theory is almost a necessary consequence of the law of definite proportions. This law holds for all combinations whether the combining substances be solid, liquid, or gaseous. But when the substances are gaseous, a still simpler law holds. We have, for example, seen that two volumes of hydrogen combine with one volume of oxygen to form water and one volume of hydrogen with one volume of chlorine to form hydrogen chloride.

143. Gay Lussac's Law of Combining Volumes. The fact that gases combine according to simple volume relations was discovered by a French scientist, Gay Lussac, and first published by him in 1808. The Law of Combining Volumes which is known as Gay Lussac's law, may be stated as follows :

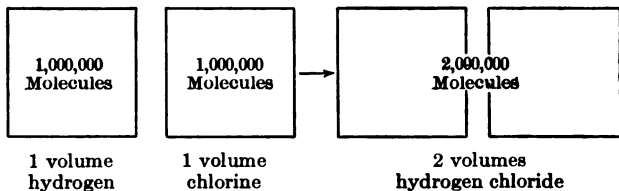
Whenever gaseous substances combine, the volumes involved are to each other in the ratio of small whole numbers: furthermore, if the product formed is also a gas, its volume is to the other volumes also in the ratio of small whole numbers.

144. Avogadro's Hypothesis. In order to account for these simple relations and also to account for the uniform

behavior of all gases under changes of temperature and pressure (Boyle's and Charles' laws) Avogadro, an Italian physicist, in 1811 proposed the hypothesis that *equal volumes of all gases under like conditions of pressure and temperature contain the same number of molecules.*

This hypothesis, however, proves inadequate if one makes the perfectly natural assumption that the molecules of the elementary gases such as hydrogen, oxygen, and chlorine consist of single atoms. Avogadro pointed out, as a necessary part of his hypothesis, that the molecules of the common elementary gases, — oxygen, hydrogen, chlorine, etc., must contain two atoms each.

145. Applications of Avogadro's Hypothesis. We know that one volume of hydrogen combines with one volume of chlorine to form two volumes of hydrogen chloride. To give a clear picture of this, let us use the following diagram, in which each of the squares represents one volume of the gas :

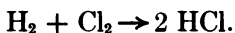


Let us assume that the one volume of hydrogen contains one million molecules of the substance.¹ The equal volume of chlorine would then contain, according to Avogadro's hypothesis, one million molecules of chlorine. The two volumes of the gaseous product must then contain two million

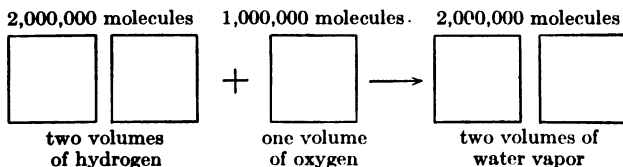
¹We say one million merely to have some definite number to work with; in point of fact the real number of molecules in a liter of hydrogen under standard conditions has been estimated to be 38,000,000,000,000,000,000.

molecules of hydrogen chloride. Now each molecule of hydrogen chloride must contain at least one atom of hydrogen, therefore there must have been at least two million atoms of hydrogen in the original one million molecules. Similarly there must have been two million atoms of chlorine in the original one million molecules of chlorine. Therefore the molecules of these elementary gases contain at least two atoms each, as Avogadro pointed out as a necessary conclusion from his hypothesis.

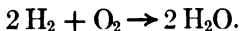
146. Chemical Symbols. It is customary in chemical notation to use symbols, and the elements are represented by single letters, or at most by two letters each, — usually the first letter of the name of the element is used. Thus H stands for hydrogen and Cl for chlorine. Furthermore, the letter H may be understood to mean one atom of hydrogen and the symbol H_2 to mean a group of two atoms, or a molecule, of hydrogen. Using these symbols, we may represent the statement that one molecule of hydrogen combines with one molecule of chlorine to give two molecules of hydrogen chloride as follows:



Again, we know that two volumes of hydrogen combine with one volume of oxygen to give two volumes of water vapor. This fact may also be expressed in terms of the hypothesis as follows:



or, reduced to simplest terms,



147. Scope of Avogadro's Theory. As we have already said in connection with the atomic theory, we must not allow ourselves to accept theory unreservedly as we do facts that are proven by the direct evidence of our senses. A theory is merely a deduction which we draw from facts with the aid of our imagination. Avogadro's theory belongs in the same category with the atomic theory, and the actual molecules, like the actual atoms, are too small to be seen or directly counted, as we could count peas in a pan of peas. We can thus scarcely hope to prove Avogadro's theory by the direct evidence of our senses. Yet, like the atomic theory, Avogadro's theory rests to-day on a great deal more evidence than that which we have given. This evidence is of so convincing a character that the theory does not fall far short of being a proven fact. Indeed, many choose to call it Avogadro's *Law*, thus signifying their belief in its absolute correctness.

148.¹ The fact that all gases behave alike under changing pressure and temperature (Boyle's and Charles' laws, Chapter VIII) had caused much speculation among scientific men, and it was in fact largely through the effort to explain these laws that Avogadro advanced his hypothesis. The necessary consequence of this hypothesis that the molecules of the elementary gases must contain two atoms appeared so improbable to the scientific men of that time that the hypothesis did not find favor until many years later. Although the physicists were ready to admit that equal volumes of gases under like condition must contain the same number of particles, neither they nor the chemists were clear as to what the particles were and the chemists were not

¹The remainder of this chapter may be omitted at the discretion of the teacher, since the understanding of later chapters does not depend on it.

then ready to admit that molecules of elementary gases could contain two atoms of the same kind.

149. Molecules of Gases must be widely Separated. When we take into consideration that water expands 1700 times when it is converted into steam, and that liquid air and other liquefied gases expand in similar degree when they change to gases, it becomes apparent that if matter really does consist of individual particles, or molecules, there must be spaces between the molecules which are very large compared with the size of the molecules themselves.

150. Nature of Heat. If the particles of a gas are so widely separated (*i.e.* when compared with their size), what can it be that keeps them apart? We know that heat causes the expansion of gases. Can it be, then, that heat is a sort of subtle fluid which flows in between the particles of a gas and thus keeps them separated? The idea does not appear absurd, but it has been decided by physicists to be incorrect. Heat is believed to be nothing but the energy of motion of the particles of a substance, moving in every direction, back and forth, within the limits set by other particles with which they are continually coming into collision.

151. Boyle's Law Explained. Gases can exert enormous pressures when they are confined, as is shown by steam in a steam engine. It is unsafe to confine liquid air in closed vessels, because, on changing to a gas, it develops such an enormous pressure as to burst any ordinary steel cylinder. The pressure is caused by the impact of the molecules of gas as they repeatedly strike and rebound from the walls of the confining vessel. The explanation of Boyle's law can now be seen: when the volume of a gas is decreased, the number of molecules in each unit of volume is correspondingly increased, and therefore the frequency of the impacts on each unit of

surface is increased. Since the impacts constitute the pressure, the pressure must increase as the volume is decreased.

152. Charles' Law Explained. Heat, as already stated, is nothing more or less than the energy of motion of the particles of a substance. The intensity of heat is measured by the temperature. Hence the intensity of the energy of the moving molecules must be measured by the temperature. The explanation of Charles' law may now be seen. The intensity of the motion of gas molecules is proportional to the absolute temperature, and thus the pressure of the gas is proportional to the absolute temperature. At the absolute zero, the gas would no longer have any pressure, because its particles would no longer be in motion. The actual volume of gas particles being not more than about one one-thousandth of the volume that the gas ordinarily occupies, it is evident that the volume would decrease to very nearly zero at the absolute zero of temperature.

SUMMARY

Gay Lussac's Law. The fact that *the ratio of the volumes of reacting gases to each other as well as the ratio of either of these volumes to the volume of the gaseous product may always be expressed by small whole numbers* was announced by Gay Lussac in 1808.

Avogadro's Theory. Avogadro, an Italian physicist, in 1811 proposed the hypothesis that *equal volumes of all gases under like conditions contain equal numbers of molecules*. This hypothesis was not well received at first, but today it is accepted as a satisfactory theory if not indeed as a law.

Applications of Avogadro's Hypothesis. As a necessary deduction from Avogadro's hypothesis, the molecules of the common elementary gases must contain at least two atoms each.

The hypothesis also furnishes a reasonable explanation for the Law of Boyle and the Law of Charles.

Heat is believed to consist of the kinetic energy of moving molecules.

CHAPTER XV

ATOMIC AND MOLECULAR WEIGHTS

153. Absolute Weights of the Atoms. The actual weight of the atoms is so exceedingly small that to give it in figures conveys but little meaning to one's intelligence. For example, it has been estimated that one atom of hydrogen weighs 0.000,000,000,000,000,000,000,0012 gram. For practical purposes, such a figure can have very little importance; furthermore, it cannot be estimated with any great degree of accuracy. But the *relative* weights of the atoms can be determined with a high degree of accuracy, and are of great importance, as we shall show in this chapter.

154. Relative Weights of the Atoms. When different elements combine, the atomic theory tells us that it is really the atoms which combine, and furthermore, that they combine in some very simple numerical proportion. What we observe is that tangible amounts of the different elements disappear in the formation of the compound; but the weights which combine must be in the same proportion or some simple multiple of the same proportion as the weights of the actual atoms.

Now we know, for example, that 35.2 grams of chlorine combine with 1.000 gram of hydrogen, and furthermore, we have decided from the volume composition of hydrogen chloride in connection with Avogadro's theory, that hydrogen and chlorine combine atom for atom. Hence the actual

atom of chlorine must weigh 35.2 times as much as the actual atom of hydrogen.

Again, we know that 7.94 grams of oxygen combine with 1.000 gram of hydrogen, in the formation of water, and we are convinced that each atom of oxygen combines with two atoms of hydrogen. Hence the atom of oxygen weighs 7.94 times as much as two atoms of hydrogen, or 15.88 times as much as a single hydrogen atom. From a comparison of these figures, it follows that the weights of the atoms of oxygen and chlorine are to each other in the ratio of 15.88 to 35.2.

155. Standard of Atomic Weights. It is perfectly clear that we need some measure by which to express atomic weights, just as the pound is a measure for expressing quantities of sugar and flour. We have seen that to give the weights of the single atoms in grams is inconvenient, as well as uncertain. But why not take the weight of the atom of some element as the standard measure? Although we do not know this accurately in terms of the measure we use for ordinary objects, we do know accurately its ratio to the weight of the other atoms, and this is all that is needed. The weight of the lightest atom, that is of the hydrogen atom, is the most logical unit to choose, because when the weights of other atoms are expressed in terms of the weight of the hydrogen atom, the numbers are all larger than one. Thus if the atomic weight of hydrogen is 1.000, the atomic weight of oxygen becomes 15.88 and that of chlorine 35.2.

The hydrogen standard for atomic weights was formerly used very generally, but at present a slight modification of this standard has been adopted by almost all chemists. Oxygen is now made exactly 16.00 instead of being taken as 15.88, and the other atomic weights are made to correspond.

This brings the figure for hydrogen to 1.008 and that for chlorine to 35.45.

The standard $O = 16.00$ is used instead of $H = 1.000$ because nearly all of the elements combine with oxygen and because most of the oxides can be weighed with great accuracy. Many of the elements do not combine at all with hydrogen, and in the case of those that do the hydrogen compounds are difficult to weigh. Thus it is apparent that oxygen is a far more practical standard for comparison.

156. Atomic Weight Determinations. To illustrate the general mode of procedure in determining atomic weights, let us imagine that we wish to determine the atomic weight of copper. We weigh a definite piece of pure copper; let us suppose that it weighs 1.0000 gram. Since, as we have just seen, oxygen is the element most used for comparison, we will seek to find what weight of oxygen is capable of combining with the copper. To do this we convert the copper into copper oxide. We must take the greatest precaution that every bit of the metal is changed and also that no particle of the metal or its compound is lost during the process. Then we weigh the copper oxide, subtract the weight of the copper which was used, and thus find the weight of oxygen which was combined with the copper. The entries which we would make in our notebooks and our calculations would appear as follows:

Weight of copper		1.0000
Weight of copper oxide		1.2517

Calculations

Weight of oxygen = difference 0.2517

Combining ratio $\frac{\text{copper}}{\text{oxygen}} = \frac{1.0000}{0.2517} = 3.973$

Atomic weight (assuming that the oxide is CuO) = $3.973 \times 16.00 = 63.57$.

Thus if we can assume that copper and oxygen are combined with each other in the proportion of atom for atom, we have found the atomic weight of copper to be 63.57. The most careful study of the compound has made it reasonably certain that this oxide contains copper and oxygen atoms in equal numbers and 63.57 is therefore accepted as the atomic weight of copper.

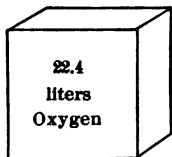
157. Molecular Weights. It is true of molecules as well as of single atoms that the actual weight is too small and too inaccurately known to be used for any practical purpose. But since molecules are made up of definite numbers of atoms, and we know accurately the weight of each of the atoms in terms of the weight of the oxygen atom taken as 16.00, — we can also express the weights of the molecules in terms of the same standard. Thus the molecular weight of oxygen, which has the formula O_2 , is $2 \times 16.00 = 32.00$, and the molecular weight of hydrogen chloride, HCl , is $1.008 + 35.45 = 36.46$.

158. Gram-Molecular Weights; Moles. Atomic and molecular weights are in themselves hardly more than abstract numbers. Thus when we say that 32.00 is the molecular weight of oxygen, we have only expressed a number which does not indicate any tangible amount of the substance. But if we say 32.00 grams of oxygen, we have specified a definite amount. Likewise, 2.016 grams of hydrogen is a definite amount of that substance. *The molecular weight in grams* of a substance is the molecular weight number taken in grams, and this quantity is so much used by chemists that the rather long expression has been shortened to the single word *mole*.

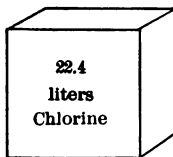
The molecule is the smallest actual particle of a substance, whereas the mole is a quantity of the substance which contains an inconceivably great number of molecules. Yet a mole of oxygen contains the same number of molecules as a mole of hydrogen, or of any other substance, however inconceivably great that number may be with respect to our ordinary powers of perception. The molecule of oxygen weighs 16 times (in round numbers) as much as the molecule of hydrogen; likewise two molecules of oxygen weigh 16 times as much as two molecules of hydrogen, and so with any greater number; thus the mole of oxygen, which contains something like 850,000,000,000,000,000,000 actual molecules, weighs 16 times as much as the mole of hydrogen which contains the same number of actual molecules of hydrogen.

Molal Volume. The *volume* of a mole of oxygen is also a quantity which is of importance. One liter of oxygen measured under standard conditions (see Chapter VIII) is known to weigh 1.4296 grams. Hence one mole, or 32.00 grams, must occupy $\frac{32.00}{1.4296} = 22.4$ liters.

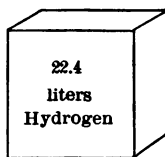
This volume is known as the *gram-molecular volume*, or simply as the *molal volume*, and it applies not only to oxygen but to all gases, because, according to Avogadro's principle, the same volume always contains the same number of molecules of a gas, whatever the gas, if the temperature and the pressure are the same.



32.00 grams, or one
mole of oxygen.



71 grams, or one
mole of chlorine.



2.015 grams, or one
mole of hydrogen.

Thus the weight of 22.4 liters of any other gas is the molal weight of that gas, and when it is desired to find what is the molecular weight of a new gas, it is only necessary to find by measurement what is the weight of 22.4 liters, since the molecular and molal weights are numerically the same.

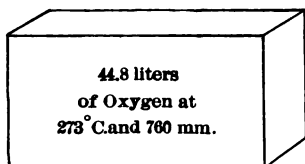
159. Molecular Weight determined by Weight of Molal Volume. Of course the amount of gas actually weighed need not be exactly 22.4 liters. For example, 100 c.c. of chlorine under standard conditions is found to weigh 0.3170 gram. The mole of chlorine would then weigh $\frac{0.3170}{100} \times 22,400 = 71.0$ grams. Hence the molecular weight of chlorine is 71.0.

160. Use of Weight of Molal Volume in finding a Formula. We have already decided to write the formula of water as H_2O . If we are correct in this, the molecular weight of water should be 18 and we should be able to test the correctness of this figure by finding the weight of the molal volume. Under standard conditions the molal volume of any gas is 22.4 liters, but water is not a gas under standard conditions. We may, however, calculate the molal volume for conditions under which water is a gas, and any temperature above 100°C ., if the pressure is 760 mm., would meet these requirements. Let us choose the temperature 273°C ., which is 546° on the absolute scale and therefore has on this scale exactly twice the value of the standard temperature of 273° absolute. The molal volume of oxygen under these conditions is given by the calculation:

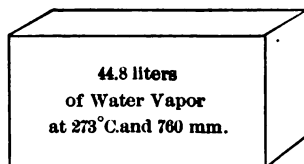
$$\text{volume (760 mm. and } 273^\circ\text{C.)} = 22.4 \times \frac{760}{760} \times \frac{546}{273} = 44.8 \text{ liters.}$$

That is, it is just twice the molal volume under standard conditions. We have now only to find the weight of water

vapor which will occupy 44.8 liters at 273°C. and 760 mm. This weight proves to be 18 grams, and thus we establish the molecular weight of water as 18 and further confirm the formula as H_2O .



32 grams, or one mole of oxygen.



18 grams, or one mole of water vapor.

161. Reason for Believing that Molecules of Common Elementary Gases do not contain more than Two Atoms. It was shown in the chapter on Avogadro's Theory that the molecules of hydrogen as well as of chlorine, oxygen, and the common elementary gases must contain *at least* two atoms each. We have tacitly assumed that they do not contain more than two atoms, and we will now show that this assumption is almost certainly correct. The proof depends on a comparison of the molal volume of the elementary gas with that of a large number of its gaseous compounds.

One molal volume of hydrogen weighs 2 grams (in round numbers), and hence the molecular weight is 2. It seems extremely probable that among all the compounds of hydrogen there are at least some in which only a single atom enters into the composition of the molecule. But a very great number of gaseous compounds of hydrogen have been studied, and none has been found in which a volume of 22.4 liters contains less than 1 gram of hydrogen. Our confidence thus becomes very great that the atomic weight of hydrogen is not less than one half of the molecular weight, or, in other words, that the molecule does not contain more than two atoms.

162. Quantitative Significance of Chemical Symbols.

Although chemical symbols serve a valuable purpose in abbreviating chemical names and thus save much time in chemical notation, this is not by any means their only usefulness. They serve also to indicate the weights of the elements in question.

Thus the formula of water, H_2O , indicates that two atoms of hydrogen are combined with one atom of oxygen in the molecule of the substance. It indicates, furthermore, that 2×1 parts by weight of hydrogen are united with 16 parts by weight of oxygen. Since the approved scientific unit of weight is the gram, the parts by weight in the formula may be taken in grams. Then H_2O signifies 2 grams of hydrogen and 16 grams of oxygen in combination, and the whole formula stands for $2 + 16 = 18$ grams, or one mole, of the compound.

163. Formulas contain Condensed Information. We have devoted a good deal of attention in foregoing chapters to the methods by which the composition of water has been found and its molecular constitution deduced. Practically all of the information so obtained is condensed in the formula H_2O . The formulas of other substances have been obtained by equally painstaking and laborious processes, but we have not the time, nor is it desirable for us, to go through all the steps for obtaining every formula that we shall use. These formulas have been derived through the labor of competent scientific men, and their labor would have been in vain if it were still necessary for every one who uses the formulas to verify them step by step. The only way in which scientific knowledge can advance is for each student to learn how to grasp the knowledge that has already been obtained, so that he can use this knowledge as a starting point in seeking to discover new truth.

Formulas condense and systematize vast funds of chemical knowledge, so that when we learn to readily interpret formulas we have at our command information which has taken years of effort to obtain.

164. Interpretation of Formulas. To understand the meaning of formulas, it is only necessary for us to remember that each symbol signifies one atomic weight of the particular element, and that each subscript means that the atomic weight of the element which the subscript follows must be taken that number of times. For example, the formula of sulphuric acid, H_2SO_4 , means that in this substance the three elements hydrogen, sulphur, and oxygen are present. Further it means that sulphuric acid contains two atomic weights of hydrogen, one of sulphur, and four of oxygen. Since the atomic weight of hydrogen is 1, that of sulphur is 32, and that of oxygen 16, it follows that sulphuric acid contains 2 parts by weight of hydrogen to 32 of sulphur and 64 of oxygen, making in all 98 parts by weight. If as is usually the custom, these parts by weight are to be taken in grams, the whole formula denotes 98 grams of sulphuric acid. In working with formulas after this manner, it is often convenient to write the numbers standing for the weights of the respective elements below the symbols, as follows:

$$\begin{array}{ccc} \text{H}_2 & \text{S} & \text{O}_4 \\ \hline (2 \times 1) + 32 + (4 \times 16) \\ 98 \end{array}$$

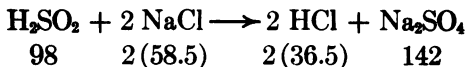
The atomic weights are understood in this fashion whenever chemical formulas are written, but ordinarily they are not thus expressed; the values for all of the elements are to be found in the table of atomic weights, a copy of which is printed inside the back cover of this book. The pupil will

find occasion to use the atomic weights of a few of the commonest elements so frequently that he will hardly fail to memorize them. A table of the most important elements is printed on page 340.

165. Equations. When chemical reactions take place, the initial substances disappear but none of the elements are destroyed; they are unchanged in quantity and remain as constituents of the new substances which appear. If the formulas of all the substances involved are known, as well as the weight of each, it is possible to write the story of the reaction in an *equation*.

The formulas of each of the initial substances are placed on the left-hand side of the equation. Each formula is taken as many times as there are formula weights. In the same way the formulas of the substances formed, taken the appropriate number of times, are placed on the right-hand side of the equation. A number placed before the formula of a substance means that the whole formula, not merely a single symbol, is to be multiplied by the number.

166. Example of an Equation. Let us, as an illustration, see how the reaction which occurs when common salt is treated with sulphuric acid at a high temperature may be expressed by means of an equation. It is known that 98 grams of sulphuric acid react with 117 grams of sodium chloride. Since the formula weights of these two substances are 98 and 58.5, respectively, the formula of the latter must be taken twice if that of the former is taken once. The products formed are hydrogen chloride and sodium sulphate, in fact 73 grams of the former and 142 grams of the latter, and these amounts are equal to two formula weights of the hydrogen chloride and to one formula weight of the sodium sulphate. We may now write the equation as follows:

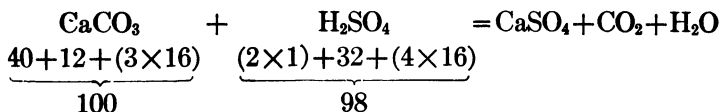


As in mathematical equations, the two sides of chemical equations are exactly equal; the laws of the conservation of matter and of the elements tell us that none of the elements can have increased or decreased in amount during the reaction. Nevertheless, it is not very customary to use the equality sign in chemical equations. Most chemical reactions are, to some extent at least, reversible; that is, they may proceed forward or backward according to varying conditions. Instead of the equality sign, then, an arrow is more often used so as to indicate the prevalent direction of the reaction.

167. Practical Bearing of Atomic and Molecular Weights.

The accurate knowledge of molecular and atomic weights is not a matter merely of theoretical interest, but it is one of immense practical importance; for, with the aid of it, chemical manufacturers can calculate the quantities of the different chemicals which they must take in their work.

For example, suppose a manufacturer of carbonated water, who is forced to prepare his own carbon dioxide, has 150 kilos of cracked marble (calcium carbonate) from which to manufacture carbon dioxide gas for charging the water (see page 60). He must find out how much sulphuric acid must be taken to react with the marble. He knows the chemical formulas of all the substances; he first writes the equation for the chemical reaction; he looks up in the table the atomic weights of the elements and adds them to give the formula weights of calcium carbonate and sulphuric acid:



So the quantities of calcium carbonate and sulphuric acid, since one formula weight of each is involved in the reaction, are in the ratio of 100 to 98. If a greater amount of one is taken, the amount of the other must be correspondingly greater. Therefore, to find the amount of sulphuric acid required in the above case, we make the proportion:

$$\frac{100}{150} = \frac{98}{x}$$

Solving: $x = 147$. Thus, 147 kilos of sulphuric acid are required to react with 150 kilos of calcium carbonate.

The weight of carbon dioxide to be obtained in the same reaction can be calculated in a similar fashion:

$$\text{CO}_2 = 12 + (2 \times 16) = 44$$

Each formula weight of calcium carbonate gives one mole of carbon dioxide. Therefore:

$$\frac{100}{150} = \frac{44}{x}$$

Solving: $x = 66$. Thus, 66 kilos of carbon dioxide are obtained.

The manufacturer might like to know what volume this carbon dioxide would occupy as a gas; he might wish to state in his advertisements how many volumes of gas were compressed into each volume of liquid. Each formula weight in grams of calcium carbonate gives one mole of carbon dioxide, which under standard conditions occupies 22.4 liters. Each formula weight in kilograms gives $1000 \times 22.4 = 22,400$ liters. Therefore,

$$\frac{100}{150} = \frac{22400}{x}$$

Solving: $x = 33,600$. Thus, 33,600 liters of carbon dioxide gas under standard conditions would be obtained.

If it were of interest to the manufacturer to calculate the weight of calcium sulphate which he could obtain, that could be done by a similar process, but ordinarily it is not necessary to know this quantity, for the calcium sulphate is a worthless product and is thrown away.

The foregoing illustrations should have made clear how extremely important is the knowledge of molecular and atomic weights for the purposes of chemical calculations. It would be advisable for the pupil at this point to practice with a number of similar calculations. He will find several problems at the end of this chapter. He should also make up problems for himself based on the substances discussed in the earlier chapters.

168. Ozone. When oxygen is subjected to the action of electrical oscillations obtained from a powerful induction coil (see Fig. 29), it is found to suffer a slight diminution

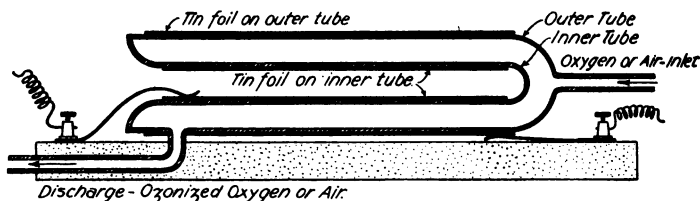


FIG. 29. — **Ozonizing Apparatus.** Air or Oxygen is passed slowly through the space between two concentric glass tubes. Electrical oscillations (but no actual passage of current) are being caused in this space, for the tinfoil conductor inside the inner glass tube and that outside the outer glass tube are connected with the terminals of an induction coil.

in volume and to acquire a strong irritating odor and a number of other properties not possessed by ordinary oxygen. For example, it will quickly darken a lustrous surface of silver or mercury, due to formation of a film of oxide. It will

bleach the color from litmus, and it will turn to a deep blue some starch emulsion to which a little potassium iodide has been added.

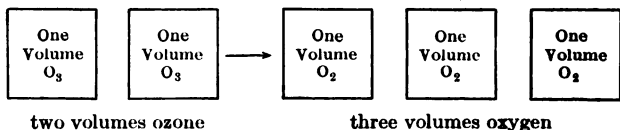
The new substance which causes these effects is called ozone, but it is composed only of oxygen. If the gas is heated to 300°C . or above, it loses all its remarkable properties; the ozone has been converted back into ordinary oxygen. At best only a rather small proportion of the oxygen (about 7 per cent) can be converted into ozone by means of electrical oscillations, but if the gas coming from the ozonizing tube is passed through a tube cooled with liquid oxygen, the ozone is condensed to an intensely blue liquid.

By allowing this liquid to boil (-119°C .) nearly pure ozone is obtained as a blue gas, but this rapidly changes until only a small per cent of ozone is left if it is allowed to rise to the room temperature. Measurements of the weight per liter of this gas at a very low temperature before it has had a chance to change to any extent into ordinary oxygen, show that the weight of the molal volume is 48 grams. What is the significance of this in the light of Avogadro's theory?

Simply that one molecule of ozone weighs $\frac{48}{32} = 1.5$ times as

much as a molecule of oxygen. Since we believe the oxygen molecule to contain two atoms of oxygen, we must conclude that the ozone molecule contains three atoms of oxygen and write the formula of ozone O_3 .

The volume change when ozone decomposes to ordinary oxygen is as follows:



Ozone is formed in small amounts in many different ways. Electric sparks through the air produce ozone, and its odor is always noticeable near the brushes of electrical machines. When an electric current is passed through dilute sulphuric acid, the oxygen escaping from the positive pole contains ozone.

Ozone is a far more vigorous oxidizer than ordinary oxygen, as shown by its action on silver and mercury. The pure ozone, either as the liquid or the gas, is explosive. These facts all show that it possesses more energy than ordinary oxygen. When it is prepared from oxygen, energy must be supplied electrically or otherwise.

Ozone is also formed in the presence of a number of substances, notably yellow phosphorus and resins, which are capable of undergoing a noticeable slow oxidation at ordinary temperatures. If a stick of freshly scraped yellow phosphorus is placed in the bottom of a glass jar and left half covered with water, the odor of ozone in the jar soon becomes very strong, and a piece of paper moistened with starch emulsion containing potassium iodide is turned blue. At the same time the phosphorus becomes covered with a dull whitish coating, because of oxidation. The energy yielded by the oxidation of the phosphorus must be used in the change of some of the surplus oxygen to ozone.

The air in pine and spruce forests is regarded as being especially invigorating, and this property is possibly due in part to traces of ozone formed in connection with the slow oxidation of the resins on the trees.

Ozone, like hydrogen peroxide, is a germicidal agent. It has been used with marked success in purifying water supplies. A little of it introduced into the air of crowded school-rooms and public halls probably has a good effect.

SUMMARY

Atomic Weights. The absolute weights of the atoms are too small to be of any practical importance. The relative weights of the atoms of the different elements, on the other hand, are of the greatest importance and can be determined with a high degree of accuracy.

These atomic weights are based on the standard of the oxygen atom, which is taken as exactly 16. By this means the hydrogen atom, which is the lightest atom, becomes approximately, although not exactly, one.

The atomic weight of an element is most often found by making a very accurate quantitative analysis of a simple oxygen compound of the element.

Molecular weights are based on the same standard as atomic weights. The gram-molecular weight of a substance is its molecular weight taken in grams; for brevity this quantity is called a mole.

Molal Volume. The volume of one mole of any gas at standard conditions is 22.4 liters. This volume is known as the gram-molecular volume or the molal volume.

To find the molecular weight of any substance that can be vaporized it is only necessary to find the weight of 22.4 liters under standard conditions, or of the molal volume calculated to the conditions of the gas if the substance does not vaporize under standard conditions.

The chemical symbol of an element signifies the atomic weight in grams of the element.

The formula of a substance signifies the formula weight in grams of the substance. Formulas contain much information in regard to the quantitative composition of the substances which they represent.

Equations tell in abbreviated form not only the different substances but the weights of the substances which take part in chemical reactions.

Ozone is an extremely active modification of oxygen. Its formula is O_3 .

Questions

1. What weights of each of the following elements are represented by the following symbols: O, H, Cl, Na, and Fe?

2. What weights of each of the following substances are indicated by the formulas H_2O , HCl , NH_3 , N_2 , and H_2SO_4 ?

3. Forty grams of sodium hydroxide are dissolved in water and neutralized with hydrochloric acid, according to the equation, $\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$. Neglecting the accompanying water, how many grams of hydrochloric acid are necessary?

4. What volume of hydrogen chloride gas under standard conditions is necessary to furnish the hydrochloric acid needed in Question 3?

5. What weight of sodium chloride would be obtained if the solution from Question 3 were evaporated to dryness?

6. Calculate the weight of barium sulphate which would be formed if 100 grams of barium chloride were treated according to the reaction, $\text{BaCl}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{BaSO}_4 + 2\text{HCl}$.

7. What volume of carbon dioxide under standard conditions would be given off if 100 grams of sodium bicarbonate, NaHCO_3 , entered into the reaction, $\text{NaHCO}_3 + \text{HCl} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{NaCl}$?

8. If 100 c.c. of ozonized oxygen is passed through a red-hot tube and then cooled to the first temperature, it is found to measure 102 c.c. What per cent by volume of the gas was ozone?

9. If one gram of liquid ozone were to evaporate, what volume would it occupy under standard conditions if none of it became changed to ordinary oxygen?

10. What volume would it occupy after 92 per cent was changed to oxygen?

11. How many cubic centimeters will 100 c.c. of air contract if it is subjected to electrical oscillations in an ozonizing tube until 3 per cent of the oxygen has been converted into ozone (21 per cent by volume of air is oxygen)?

12. Refer to statements as to composition of hydrogen peroxide on page 108 and decide what is the formula of the substance.

13. In what respects are hydrogen peroxide and ozone similar in their properties?

CHAPTER XVI

CHLORINE

It was stated in Chapter XIII that chlorine is obtained from hydrochloric acid by oxidizing away the hydrogen of the latter by means of manganese dioxide. Using now the knowledge of chemical abbreviations gained in the last chapter, we can express this reaction by means of the equation:



This equation shows that water is formed by the union of the hydrogen and oxygen, manganese chloride is formed, and half of the chlorine from the hydrochloric acid is set free.

169. Source of Chlorine. The source of hydrochloric acid, and in fact of most of the chlorine of commerce as well as most of the chlorine compounds, is common salt. Sodium chloride is present in the water of the ocean to the extent of about 2.65 per cent. It is also found in vast deposits in many parts of the earth where formerly there have existed salt lakes, or bays, the water of which has evaporated, leaving solid salt.

In the course of ages these deposits have frequently become covered with earth and buried deeply beneath the surface. Such salt beds may be worked by mining, or, more often, by sinking pipes through which water may be introduced to the deposit. When the water becomes saturated

with salt, it is pumped up again and evaporated to obtain the dry salt. There is a great advantage in evaporating this concentrated brine, which contains nearly 40 per cent of salt, instead of sea water, which contains less than 3 per cent.



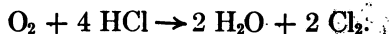
FIG. 30. — Vats for Evaporating Brine in Salt Industry.

Consequently, sea water is not much used as a source of salt except in very warm and sunny climates.

170. Deacon's Process. On the large scale, instead of using the oxygen of manganese dioxide to oxidize the hydrogen of hydrogen chloride, an ingenious method of using the oxygen of the air was devised by Deacon in 1868. Although the free oxygen of the air will not oxidize hydrogen chloride under ordinary conditions, it will do so when the conditions are made right. A careful study, by methods which we shall not attempt to discuss fully, has proved that oxygen has a greater chemical attraction for hydrogen than chlorine has, and thus it is only to be expected that oxygen should be able to withdraw hydrogen from its combination with chlorine.

Under ordinary conditions this attraction is not apparent, any more than the attraction between oxygen and charcoal in the cold.

When, however, hydrogen chloride gas and air are mixed and drawn through heated tubes containing copper chloride, a reaction takes place and chlorine is liberated freely :



The copper chloride is not changed by this reaction ; it acts therefore merely as a catalyzer, just as does the manganese dioxide in the preparation of oxygen from potassium chlorate (see page 40). In order that the copper chloride shall work efficiently, a large surface of it must be exposed to the mixture of gases. This is accomplished by saturating some porous material, such as pumice stone, with a solution of the copper salt and then drying it. This method of obtaining chlorine from hydrogen chloride is known as Deacon's process.

171. Electrolysis of Brine. At the present day a large part of the chlorine of commerce is made by the electrolysis of common salt solution. The chlorine is given off at the positive pole ; at the negative pole sodium hydroxide is formed, while hydrogen gas escapes.

When dry sodium chloride melted by intense heat is electrolyzed, chlorine and sodium are obtained. The attraction which holds sodium and chlorine in combination is overcome by means of the electric current. Since we know that sodium reacts rapidly with water,



the formation of sodium hydroxide at the negative pole when the water solution is electrolyzed is easily understood.

Thus by the electrolytic process another valuable product

is obtained besides the chlorine. Such a product other than the chief one sought is known as a by-product. Many commercial processes of to-day yield large profits from their by-products, and often thereby the price of the principal product is materially lessened.

172. Laboratory Preparation of Chlorine. To prepare chlorine in the laboratory for the purpose of studying its properties, the older method of oxidizing hydrochloric acid with manganese dioxide is suitable. Manganese dioxide in small lumps is placed in a generator flask like that used in preparing hydrogen chloride (see Fig. 25). Enough hydrochloric acid is poured in through the thistle tube to seal the latter and cover the manganese dioxide. A reaction begins at once, but to yield a free supply of chlorine the flask may be cautiously warmed with a Bunsen flame.

Chlorine gas cannot well be collected over water, as it dissolves to some extent in the latter. It may be led through a delivery tube to the bottom of a bottle. When the bottle is filled with the greenish-yellow gas, a glass plate is placed over the top to prevent the gas from diffusing out.

All work with chlorine should be done under a hood with a strong draft, so that none of this offensive gas which escapes from the generator and from the bottles may get out into the laboratory.

173. Physical Properties. Chlorine is a gas of a pale yellowish-green color. It has an offensive and suffocating odor. When inhaled, even in minute quantities mixed with air, it is very irritating to the mucous membranes; when at all concentrated, it is most dangerous to inhale. One volume of water dissolves a little more than two volumes of chlorine; the solution is yellow and smells strongly of chlorine. Chlorine is about two and one half times as heavy as air. The dry

gas is much more easily liquefied than air; at atmospheric pressure it is liquid at $-34^{\circ}\text{C}.$; at ordinary temperature it is liquefied by higher pressure, seven atmospheres sufficing at $20^{\circ}\text{C}.$

174. Chemical Properties. Chlorine does not burn in the air, neither is it a supporter of the combustion of ordinary fuel materials. A lighted taper thrust into a bottle of chlorine is extinguished. Nevertheless, chlorine can, like oxygen, combine with almost all of the other elements, and, with some of them, with considerable violence. For example, if a little powdered antimony is dropped into a jar of chlorine, a brilliant shower of sparks is instantly produced.

175. Chlorine and Metals. Likewise, iron, zinc, and copper, if very finely powdered so that a large surface is presented for the chemical action, ignite spontaneously in chlorine. The combustion of these, as well as of other metals in chlorine, yields the chlorides of the metals. Thus, sodium chloride is formed when sodium is burned in chlorine, whereby our conclusion already made that common salt is composed of chlorine and sodium receives further confirmation.

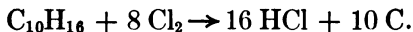
176. Chlorine and Hydrogen. Chlorine has a strong tendency to combine with hydrogen. As already stated (page 118), a jet of hydrogen burns in a jar of chlorine; likewise, a jet of chlorine will burn in a jar of hydrogen. An explosive mixture is formed by chlorine and hydrogen, just as detonating gas (see page 115) is formed by oxygen and hydrogen, and this mixture is naturally most explosive when it contains the two gases in the proportion in which they combine, that is, volume for volume.

Such a mixture is made to explode even more easily than the oxygen-hydrogen mixture. To illustrate this let us fill a thin glass bulb in a shaded corner of the laboratory with a

mixture of equal volumes of chlorine and hydrogen. Then, for protection, support a pane of thick plate glass between the bulb and the observer and bring the whole into the direct rays of the sun. A deafening explosion occurs immediately. The light from a magnesium flashlight powder is also sufficient to explode the mixture.

This experiment does not necessarily show that chlorine is stronger than oxygen in its chemical affinity for hydrogen, for we have already stated (page 165) that the exact contrary is the case; the fact that the attraction of the oxygen is really greater is shown in that the oxygen-hydrogen mixture explodes with more violence and develops more heat thereby. Starting an explosion is something like pulling the trigger of a rifle; the pull necessary to release the hammer gives little indication as to the power of the rifle.

The affinity of chlorine for hydrogen is further shown in the behavior of turpentine, which is a compound consisting of only hydrogen and carbon. If a piece of filter paper is wet with hot turpentine and then lowered into a jar of chlorine, a flash followed by the escape of dense black smoke occurs. The chlorine has combined with the hydrogen of the turpentine and left the carbon uncombined to appear as the black smoke:



That hydrogen chloride has also been formed is indicated in that a strip of litmus paper is turned red when it is moistened and then lowered into the jar.

177. Chlorine and Carbon. The last experiment would also indicate that chlorine does not unite directly with carbon, which is much in line with the fact that ordinary fuels do not burn in chlorine. Carbon does, to be sure, form compounds

with chlorine, of which the most important is carbon tetrachloride, CCl_4 , a liquid substance that is well known and extensively used as a solvent and as a fire extinguisher. These compounds are not made, however, by direct synthesis from the two elements.

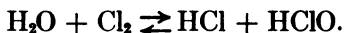
178. Chlorine Water. For many purposes chlorine reacts more satisfactorily in water solution than in the form of the dry gas. Such a solution is known as chlorine water. It reacts with the precious metals which are not affected by ordinary acids. Thus a piece of gold leaf is at once dissolved by chlorine water. The chlorine combines directly with the gold, forming chloride of gold, and the latter is soluble in water.

179. Aqua Regia. Chlorine may be liberated from hydrochloric acid by oxidation with nitric acid. A mixture of three volumes of concentrated hydrochloric acid and one volume of concentrated nitric acid is in the correct proportion, and such a mixture is known as aqua regia (literally, kingly water) because it continually liberates chlorine, which causes the precious metals to form soluble chlorides and thus appear to dissolve. Aqua regia is used by jewelers and chemists when gold and platinum are to be converted into soluble compounds.

180. Bleaching. The most important use of free chlorine is in bleaching linen and cotton fabrics. The natural fibers when woven into cloth present a pale yellow or greenish-brown tinge, and this is destroyed by the bleaching, leaving the goods pure white.

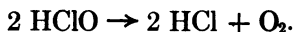
Chlorine water itself is unstable, as is shown by the fact that it loses its yellow color in a few hours or, at most, days. It is, however, this very instability which gives it its power to bleach.

When chlorine is dissolved in water, a small portion of it interacts to form hydrochloric and hypochlorous acids :



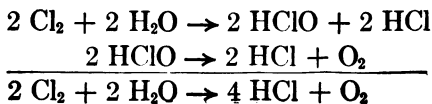
When a small amount of these products is formed, the reaction ordinarily stops, because whenever any considerable amounts of these products are brought together, they react to form chlorine and water. Thus in the above equation arrows are made to point in both directions because the reaction may go either way, according to conditions. What we call chlorine water thus contains hydrochloric acid and hypochlorous acid in addition to the chlorine and water.

181. Instability of Hypochlorous Acid. Hypochlorous acid is a most unstable substance, and it gives up its oxygen to oxidizable substances with extreme ease. In fact, in the sunlight, it breaks down rather rapidly of itself :



Thus, if we invert a test tube of chlorine water in a beaker of the same solution and allow the whole to stand in the sunlight, we find in an hour or so that the yellow color of the chlorine has gone and that in the test tube a few bubbles of a gas, which proves to be oxygen, have collected. As fast as the hypochlorous acid is taken out of the way through the decomposing agency of the sunlight, the reaction of the chlorine with the water progresses further, since the tendency to oppose this reaction is now removed. Thus all the chlorine ultimately disappears.

The total change effected by the succeeding reactions sums up as follows :

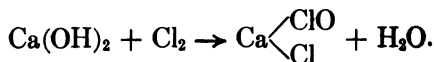


or expressed in words, chlorine has displaced the oxygen from water. This is the direct opposite of what takes place in the Deacon process, but it is to be noted that this reaction takes place in water solution, whereas the Deacon process was carried out with the dry gases. Such a difference of conditions oftentimes occasions an entire change in the direction of a reaction.

182. Theory of Bleaching. Dry chlorine gas is incapable of bleaching dry fabrics, as is easily shown by suspending a piece of colored calico in a bottle of dry chlorine. Wet the cloth, however, and lower it again into the chlorine and it is very soon decolorized. Most dyestuffs, both the coal-tar dyes, which are principally used in coloring cotton goods, and the yellow and brown coloring matter of the natural fibers, are very complex compounds containing carbon and hydrogen and often nitrogen and oxygen. Very slight changes in their make-up, such as the addition of a little oxygen, often completely change the color, and most often remove it altogether. It is generally supposed that bleaching really consists in adding oxygen to the dyestuff molecule. The instability of hypochlorous acid furnishes what is practically atomic oxygen ready to add directly to the dyestuff:

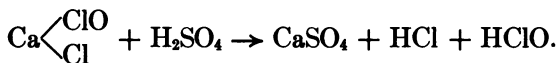


183. Bleaching Powder. Chlorine gas itself is most disagreeable and dangerous to handle and is difficult to transport and store. For bleaching purposes, it has therefore been customary to absorb the chlorine in calcium hydroxide, with which it reacts to form what is known as bleaching powder:



This substance is a dry powder; it can be kept indefinitely without decomposition, and can be handled and transported without danger.

When it is to be used for bleaching, it is stirred up to a very thin paste with water and placed in vats, through which the goods are run over mechanical rollers (Fig. 31). The bleaching powder itself is rather ineffective when compared with hypochlorous acid, but it readily gives hypochlorous acid when treated with sulphuric acid:



It is not advisable, however, to mix the bleaching powder and the sulphuric acid all at once. The roll of cloth after

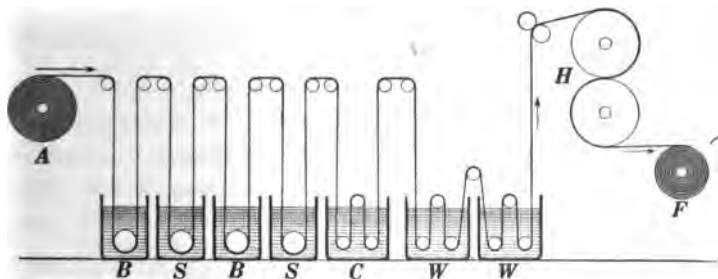


FIG. 31.—Bleaching. A, unbleached goods on roll; BB, vats of bleach liquid; SS, vats of dilute sulphuric acid; C, vat of sodium sulphite; WW, water for washing cloth; H, steam heated roll; F, roll for the bleached goods.

passing through the bleach vat is next passed through a vat containing very dilute sulphuric acid. Thus the hypochlorous acid is produced only within the fibers of the cloth where it will be effective.

In the diagram, the roll of goods is represented as being passed alternately through two bleach vats and two sulphuric

acid vats, then through a bath of sodium sulphite to destroy any hypochlorous acid which would otherwise rot the goods, then through a washing bath of water, and lastly over steam-heated cylinders to dry and iron the cloth.

Bleaching powder is also known as chloride of lime, and under this name it is extensively sold in small cans for use as a deodorizer and disinfectant. It has an intense and to most people disagreeable odor which to some extent resembles that of chlorine. The odor is really that of hypochlorous acid, a little of which exists even in the unacidified bleaching powder. Its deodorizing power comes from the same cause as its bleaching power, namely, the readiness with which it gives off oxygen to oxidizable material. Noxious matter is, for the most part, readily oxidizable, and by oxidation is converted into harmless substances. As a disinfectant, bleaching powder kills disease germs.

184. Liquid Chlorine. At present much chlorine is condensed to the liquid condition and stored and shipped in strong steel cylinders instead of being absorbed by slaked lime. Such chlorine is very convenient for use by skilled workmen, but the bleaching powder is safer. In some towns, liquid chlorine, bought in ton lots, is being used to render the municipal water supply safe for drinking purposes.

185. Comparison of Oxygen and Chlorine. In its general chemical nature, chlorine is extremely like oxygen. It is a characteristic non-metal and unites with all the metals, forming chlorides, just as oxygen forms oxides. In the chlorides and oxides, chlorine and oxygen are mutually interchangeable; one atom of oxygen, however, is equivalent to two atoms of chlorine. Under most conditions, the chemical affinity of oxygen is somewhat greater than that

of chlorine, and oxygen can drive chlorine out of its compounds more easily than chlorine can displace oxygen. In its power to combine with carbon, oxygen stands considerably ahead of chlorine, but, on the other hand, chlorine excels oxygen in its ability to form compounds with the precious metals.

SUMMARY

The chief source of chlorine and all chlorine compounds is common salt, which is the most abundant material containing chlorine.

Free chlorine is obtained by oxidizing the hydrochloric acid obtained from salt. The hydrogen forms water with oxygen, while the chlorine is left uncombined.

But by far the greatest part of the chlorine used commercially is obtained by electrolyzing common salt solution. By this process, sodium hydroxide is obtained as a by-product.

Properties of Chlorine. Chlorine is a greenish-yellow gas, heavier than air, and somewhat soluble in water. It is irritating to the breathing passages and is dangerous if inhaled in quantity.

Chemically, chlorine is a very active non-metallic element, resembling oxygen in this respect. It forms compounds with almost all of the other elements. Towards hydrogen, carbon, and the majority of the elements, it is somewhat less active than oxygen; towards the precious metals, however, it is more active.

The principal use of chlorine is based on its indirect bleaching of organic coloring matter. This property depends upon the release of oxygen from water by the action of chlorine, this released oxygen being in a condition to enter into reaction far more easily than atmospheric oxygen.

For practical bleaching purposes, chlorine itself is not much used, but rather bleaching powder, which is obtained by allowing chlorine to react with calcium hydroxide. Some chlorine, however, is compressed to the liquid condition in strong steel cylinders, for transportation and use.

Questions

1. What compound occurring in nature is the chief source of chlorine? Describe two totally different methods by which free chlorine may be obtained from it.
2. In obtaining salt on the large scale, why is brine from salt wells used rather than sea water?
3. What becomes of the sodium of the salt in each of the methods by which chlorine is obtained?
4. How could you identify chlorine without making use of the properties of odor or color?
5. Give three reasons for considering oxygen a somewhat more active non-metallic element than chlorine.
6. What uses has chlorine, in a practical way?
7. Give reasons for thinking that the bleaching of organic coloring matter is a process of oxidation.
8. What weight of manganese dioxide must be used to liberate chlorine from 100 kilograms of 36.5 per cent hydrochloric acid according to the reaction $4 \text{HCl} + \text{MnO}_2 \rightarrow \text{MnCl}_2 + 2 \text{H}_2\text{O} + \text{Cl}_2$?
9. What weight of chlorine will be obtained in Question 8?
10. What volume will the chlorine obtained in Question 9 occupy under standard conditions?
11. If we start with the 100 kilograms of 36.5 per cent hydrochloric acid used in Question 8, and could use sulphuric acid and manganese dioxide, what is the maximum amount of free chlorine that could be obtained? Write the equation and compute the amounts of sulphuric acid and manganese dioxide that would be required.
12. How would you treat bleaching powder in order to obtain chlorine gas? Give equations.

CHAPTER XVII

SODIUM

IN the preceding chapter, we have discussed chlorine, a non-metal which is one of the constituents of common salt. The other constituent of salt is sodium, a metallic element. Sodium is a different sort of metal from iron, zinc, copper, and those metals that are used in everyday life.

In the first place, we never see sodium in everyday life because it is such a chemically active substance that it cannot be kept in contact with the atmosphere. A little piece of sodium left uncovered in a dish immediately loses its bright metallic appearance and turns dull, shortly a white crust forms which continually swells up with little bubbles, until at last the whole lump seems to liquefy. This change is due to the reaction of sodium with the water vapor of the atmosphere. We have already seen (Chapter X) that sodium reacts rapidly with cold water, displacing hydrogen from the latter.

186. Preparation of Sodium. When melted sodium chloride is decomposed by electrolysis, sodium is set free at the negative pole, at the opposite pole from that at which the chlorine is liberated. But it is a difficult matter to keep sodium chloride at a high enough temperature to melt it and thus enable the electrolysis to take place. Solid salt is a non-conductor of electricity and thus cannot be electrolyzed.

In the actual preparation of sodium by electrolysis, sodium hydroxide, NaOH , commonly called caustic soda, is used, because this melts at a fairly low temperature. When this is electrolyzed, oxygen is evolved at the positive pole and sodium and hydrogen are both formed at the negative pole. The hydrogen escapes, and the sodium which is molten at the temperature of the bath, is drawn off and allowed to solidify in appropriate molds. The sticks of sodium so prepared are preserved under kerosene or similar oil to protect them from the atmosphere.

187. Physical Properties. Sodium has a silver-white color and a metallic luster. In its possession of this metallic luster and in its ability to conduct electricity, it resembles all other metals. In other respects it has quite different physical properties from those that the everyday man associates with metals. Thus it is very soft; it can be cut with a knife almost as easily as cheese; it is so light that it floats on water, and it melts below the temperature at which water boils.

188. Chemical Properties. Chemically, sodium differs from the common metals in its extremely great activity. As we have seen, it rapidly decomposes cold water, liberating hydrogen. It burns intensely in air, forming sodium peroxide. It does not, however, ignite spontaneously, because it becomes covered with a thin coating of oxide which protects the metal underneath. We have already seen that sodium combines with chlorine as well as with oxygen; in fact, sodium has a very strong tendency to unite with all the non-metallic elements.

Being itself far more active than most of the other metals, sodium is capable of displacing the latter from their compounds just as it displaces hydrogen from water. For

example, metallic aluminium is formed when aluminium chloride and metallic sodium are heated together. The sodium takes the chlorine away from the aluminium, whereby sodium chloride is formed. Likewise, sodium can remove the oxygen from the oxide of any less active metal.

COMPOUNDS OF SODIUM

189. Sodium Chloride, or Common Salt, NaCl. Besides being the chief source of chlorine, common salt is also the chief source of sodium. Salt also is as useful a substance as it is abundant. The human blood contains 0.8 per cent of sodium chloride.

Although necessary in small amount in the food, too much salt is harmful and even dangerously poisonous. Shipwrecked sailors perish of thirst because they cannot drink salt water. Salt in any quantity is also harmful to the lower organisms that cause putrefaction and decay. Hence the use of salt as a preservative for meats, for fish, for hides, etc.

Salt is easily soluble in cold water, but, unlike most substances, it is but slightly more soluble in hot water. When the water of the solution is evaporated, the salt crystallizes in cubical crystals. These crystals when perfect are true cubes, but it is seldom that the faces are evenly developed. We frequently find the salt growing in hopper-shaped crys-

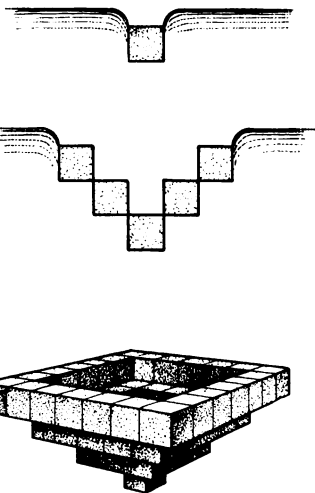


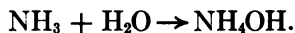
FIG. 32. — Hopper-shaped Salt Crystals.

tals. Figure 32 shows the formation of an idealized hopper crystal.

190. Sodium Bicarbonate, or Baking Soda, NaHCO_3 . This substance has been mentioned in the chapter on carbon dioxide (pages 59 and 61) as the material which is used to supply that gas in fire extinguishers and in baking powder. The sodium which sodium bicarbonate contains is derived from sodium chloride; the carbon dioxide may be obtained by heating limestone (see page 51, also see next chapter).

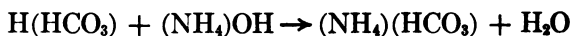
The process of manufacturing sodium bicarbonate is carried out as follows: A saturated solution of sodium chloride containing about 36 grams of sodium chloride to 100 grams of water is first prepared. This is saturated with ammonia and then carbon dioxide is passed into it. Sodium bicarbonate, which is sparingly soluble, thereupon precipitates out in the solid form, and after it is drained, washed, and dried, it is ready to be marketed.

The reactions occurring in this process are of interest. First, ammonia unites with water to form ammonium hydroxide.



Ammonium hydroxide is a base, and bases are exactly opposed in chemical nature to acids.

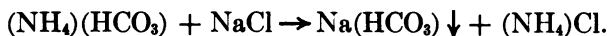
Next, carbon dioxide dissolves and reacts with water to form the weak carbonic acid. It is characteristic of bases and acids that they mutually neutralize each other and thereby form a salt and water. Thus the carbonic acid is neutralized by the ammonium hydroxide:



and the salt ammonium bicarbonate is formed.

Now this salt and sodium chloride are both fairly soluble

in water. Any two salts in solution are capable of interchanging their component parts, or radicals. These two may interchange in this way, whereby ammonium chloride and sodium bicarbonate are formed. If both of these new salts were as soluble as the former, no change would be seen by an observer, but in fact the sodium bicarbonate is only sparingly soluble and hence it precipitates out as a powdery solid.



The arrow pointing downward signifies that the substance precipitates.

This process is called the Solvay process, and it is carried on extensively at Syracuse, New York, where an abundant supply of concentrated brine is supplied by salt wells. The amount of salt drawn from the wells amounts to several hundred tons, daily.

In order for this process to be possible from a commercial standpoint, it is necessary to work up the ammonium chloride left in the solution so that all of the ammonia may be recovered from it and used over again in the process.

Sodium bicarbonate is easily decomposed by heat and it gives off some carbon dioxide if thrown into boiling water. It is completely decomposed by acids so that a large amount of carbon dioxide is evolved. On this property depends the use in baking powders and fire extinguishers. When decomposed by the acid, it in turn neutralizes the acid. Thus sodium bicarbonate is a good deal used to neutralize acids where it is essential not to use any substance which on its own part is corrosive. For example, it is used to relieve burns on the flesh, as an eyewash when the eyes are inflamed and develop an acidity, and internally as a corrective for sour stomach.

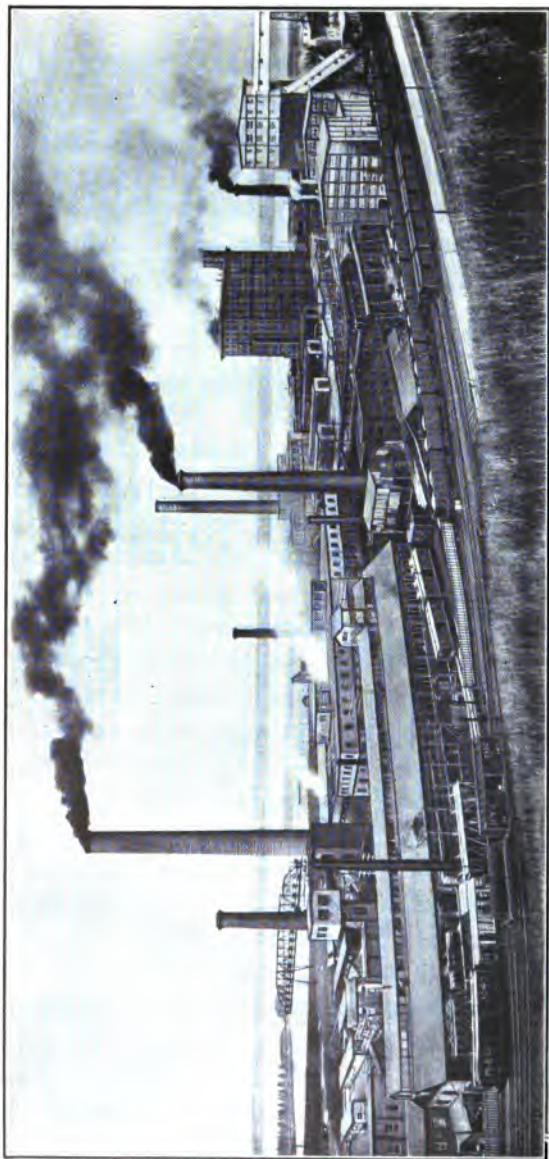
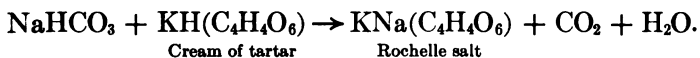


Fig. 33. — A Part of the Solvay Works, Syracuse, N. Y. The three chimneys, from furnaces where the sodium bicarbonate is calcined, show no smoke because they have automatic stokers and large combustion chambers.

191. Baking Powder. The majority of baking powders contain sodium bicarbonate, together with some mildly acid solid substance such as cream of tartar, or calcium acid phosphate, or alum. On wetting the mixture immediate reaction results, whereby a large volume of carbon dioxide is released. If the powder has been previously well blended with the flour the carbon dioxide is scattered throughout the loaf and leavens it. Some other harmless product always remains in the dough. In the case of a cream of tartar powder, potassium sodium tartrate (Rochelle salt) is the product, as is shown by the following equation for the reaction between cream of tartar and bicarbonate of soda.



192. Sodium Carbonate, or Washing Soda, Na_2CO_3 . A large quantity of the sodium bicarbonate manufactured by the Solvay process is used as such, but a far greater quantity is converted into sodium carbonate, Na_2CO_3 . On heating, the bicarbonate decomposes into the carbonate while water vapor and carbon dioxide are evolved.



The arrows pointing upward indicate that the substances escape as gases. The carbon dioxide thus freed is returned into the Solvay process for the conversion of more sodium chloride into bicarbonate.

Sodium carbonate is also called washing soda because this name describes one of its important household uses.

Sodium carbonate acts as a mild alkali, one indication of this being that it colors litmus blue in distinction to acids, which color it red. The use of sodium carbonate for cleansing purposes depends on its alkaline character, for alkalies

possess the power of loosening grease and dirt and thus allowing of their removal with water. Sodium carbonate is sufficiently alkaline for the purpose and yet not so alkaline as to injure seriously the flesh or fabrics or woodwork. Caustic soda, on the other hand, is too powerful an alkali to use in cleaning, for besides removing dirt, it attacks the flesh strongly and it disintegrates woolen fabrics and wood.

The alkaline character of sodium carbonate is further exhibited in its power to neutralize acids. Except for very delicate neutralizations, it is used for this purpose more extensively than sodium bicarbonate. Its action is similar to that of the latter, in that a neutral salt, water, and carbon dioxide are formed.



But it will be noticed on comparing the reactions that only one half as much carbon dioxide escapes for the same amount of acid neutralized.

Sodium carbonate has a multitude of industrial uses which for the most part depend on its alkalinity and its ability to neutralize acids. Enormous quantities also are used to manufacture sodium hydroxide or caustic soda, in the manufacture of soap, and in the manufacture of glass.

193. Soda Crystals, $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$. Much of the sodium carbonate of commerce is put on the market as a dry powder of the formula Na_2CO_3 . But another large part is sold as so-called soda crystals which consist in fact of transparent crystals which contain ten molecules of water in addition to the sodium carbonate proper, as is indicated in the above formula.

When a solution of sodium carbonate in water is allowed to crystallize at a low temperature, the solid that separates

contains ten moles of water for each formula weight of sodium carbonate. This is regarded as a true chemical compound, for it always contains sodium carbonate and water in exactly the same proportions. Furthermore, the crystals are totally different in structure from anhydrous sodium carbonate (that is, Na_2CO_3 without water) or from ice (that is, crystallized water). The chemical affinity binding the water and the sodium carbonate together is, however, much weaker than that which holds the hydrogen and oxygen together in water, or the sodium, carbon, and oxygen in the sodium carbonate.

That the water is bound very loosely to the salt in the crystals is shown by the fact that it can all be driven off with very gentle heating, thus leaving the salt anhydrous. In fact, this decomposition takes place slowly even at ordinary temperatures, and the crystals crumble to a white powder consisting of the more or less dehydrated substance.

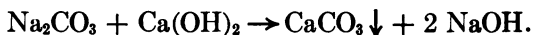
194. Crystal Hydrates and Efflorescence. When crystals of this type decompose spontaneously in this way, they are said to *effloresce* (literally to bloom) because the powder frequently resembles masses of snowy blossoms.

Water held in combination with a salt in crystal form is known as *water of crystallization*. Such salts are called *crystal hydrates*. A great many salts besides sodium carbonate possess the power of thus taking on water of crystallization.

195. Sodium Hydroxide, or Caustic Soda, NaOH . This substance is obtained in the solution when metallic sodium reacts with water and displaces one half of the hydrogen. It is made commercially by the electrolysis of sodium chloride solution. Probably the largest part of the sodium hydroxide used is made by causticizing sodium carbonate.

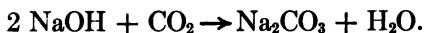
In the last-mentioned method, the source of the sodium is sodium carbonate and that of the hydroxide radical is cal-

cium hydroxide (see next chapter). The success of this method depends on the fact that the unwished-for constituents, that is, the carbonate radical and the calcium, form together a very insoluble substance, calcium carbonate, which precipitates, and thus can be separated from the sodium hydroxide remaining in solution :



To carry out the process, a solution of sodium carbonate is thoroughly mixed with calcium hydroxide. The precipitate is allowed to settle and the clear liquor containing the sodium hydroxide is drawn off. This liquor is boiled in iron pots until all the water is driven off, when pure sodium hydroxide is left as a melted substance. This is then poured off into molds or into large iron drums, in which it solidifies.

Sodium hydroxide is a white solid substance which is extremely soluble in water. It melts very easily at a temperature below a visible red heat. It has a great attraction for water, as is shown by the experiment of leaving a small lump of sodium hydroxide exposed to the air. The surface of the lump almost immediately becomes moist and soon the whole lump appears to liquefy. The sodium hydroxide dissolves in the water which it absorbs from the atmosphere. Moist sodium hydroxide also absorbs carbon dioxide with great avidity and thereby forms sodium carbonate.



Thus if a lump of sodium hydroxide is left exposed for a long time to the air, it is ultimately all changed to carbonate because the air contains a minute amount of carbon dioxide — much less, however, than it does of water vapor.

In Chapter IV, the experiment of absorbing the products

of burning a candle by means of sticks of caustic soda placed in a lamp chimney was described. It is now obvious that this absorption takes place because the combustion products consist entirely of water vapor and carbon dioxide.

Great quantities of sodium hydroxide are used in the industries wherever a very strong alkali is required; especially is it used in soap making, in petroleum refining, and in preparing coal-tar products.

196. Sodium peroxide, Na_2O_2 , is made by burning metallic sodium in the air. It is itself a powerful oxidizing agent, for it contains twice as much oxygen as the ordinary oxide, Na_2O , and the extra oxygen is given up with ease to oxidizable substances. Sodium peroxide yields hydrogen peroxide when it is treated with an acid.



Hydrogen peroxide is useful as an oxidizing agent in general and particularly as an antiseptic and as a bleaching agent for silk and wool.

A convenient method for preparing oxygen in the laboratory is to treat sodium peroxide with water. Probably hydrogen peroxide is first formed and then decomposed into water and oxygen by the high temperature resulting from the heat of the reaction.

197. Sodium Nitrate, NaNO_3 — Chili Saltpeter. This compound of sodium is found in immense deposits in Chili in South America. It is a valuable fertilizer — furnishing nitrogen in a soluble form, and hence readily available for plant food. Sodium nitrate is also the raw material from which most of the nitric acid of commerce is made.

198. Flame Test for Sodium. Sodium is remarkable for the intense pure yellow light which the vapor of the metal



FIG. 34. — Packing Sodium Nitrate in Chili.

or of its compounds imparts to a flame. When a clean platinum wire is held in the colorless flame of a Bunsen burner, no effect is noticed. If the wire is dipped into a solution of sodium chloride or any sodium compound and then held in the flame, the latter is colored intensely yellow. The minutest trace of sodium causes this coloration, and so this *flame test* is valuable as a means of detecting the presence of this element.

199. Potassium is an element which is extremely like sodium. In fact, all that we have said about sodium would apply almost equally well for potassium. Potassium is even a little more active than sodium; it decomposes water with even more violence.

200. Natural Occurrence of Sodium and Potassium. All of the simple compounds of both sodium and potassium are easily soluble in water. Hence sodium chloride is found in

such abundance in sea water. The rain washes it from the land into the sea. Sea water contains potassium salts also but in much smaller amount. Many rocks contain both sodium and potassium. For example, the minerals feldspar and mica contain either one or both of these metals in the

form of double silicates with aluminium. As the rocks slowly disintegrate under the action of the frost, the rain,

and the carbon dioxide of the air, the potassium and sodium become

washed out as soluble carbonates. On percolating through the soil these salts become changed before long into nitrates or chlorides of the metals. Potassium salts are essential to the growth of plants, and much of the potassium thus washed from the disintegrated rocks is taken from the soil by the roots of plants. On the other hand, the greater part of the sodium is washed on into the ocean.

201. Glass. Sodium and potassium are essential constituents of glass, which is a double silicate of either sodium or potassium on the one hand and of calcium or lead on the other hand. Common window glass, for example, is a sodium and calcium silicate of approximately the composition,

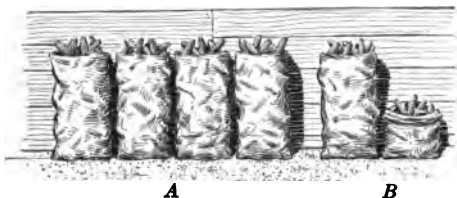


FIG. 35. — Results of Using Potassium Salts as Fertilizer. *A*, fertilized with 200 lb. Muriate of Potash per acre; yield per acre, 73.4 bushels. *B*, without fertilizer; yield per acre, 32.1 bushels. These experiments were conducted side by side on soil containing otherwise sufficient plant food.

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Glass is comparatively easy to melt as compared with most natural silicates, and when it cools, it remains transparent

while it hardens. Like feldspar, mica, and other natural silicates, glass is almost insoluble in water, but it must be remembered that glass, too, like them, is a complex compound, whereas all of the simple compounds of both sodium and potassium are comparatively very soluble.

SUMMARY

Common salt is composed of chlorine and sodium, the former a non-metal, the latter a metal.

Metallic sodium is obtained by the electrolysis of sodium chloride, or better, by electrolysis of sodium hydroxide.

Properties of Sodium. Sodium differs from the more common metals in that it is far more active. It unites with all non-metals. It displaces hydrogen from water and metals from their compounds. Sodium is very soft; it is light in weight, and it melts below the boiling point of water. It possesses, however, metallic luster and conductance for electricity, which are properties that belong to all metals.

Important compounds of sodium are: sodium chloride, NaCl , a neutral salt; sodium bicarbonate, NaHCO_3 , a compound which finds use in neutralizing acids and in the production of carbon dioxide; sodium carbonate, Na_2CO_3 , a salt which is mildly alkaline and used as a washing powder; sodium hydroxide, NaOH , which is very strongly alkaline; sodium peroxide, Na_2O_2 , which is a strong oxidizing agent and a source of hydrogen peroxide; and sodium nitrate, NaNO_3 , a valuable fertilizer and source of nitric acid. Baking powders usually contain sodium bicarbonate, together with some mildly acid solid substance such as cream of tartar.

Potassium is a metallic element extremely like sodium in properties. It is more active than sodium.

All simple compounds of sodium and potassium are easily soluble in water. These elements, however, are essential constituents of glass and of minerals like feldspar and mica, which are practically insoluble, but in many years the slow weathering of rocks does wash out the salts of sodium and potassium.

Questions

1. Why is common salt rather than some other naturally occurring compound used to prepare sodium compounds?

2. Explain the use of baking soda in connection with sour milk in raising dough.

3. Which would be more economical to buy, washing soda that had stood in an open barrel for a month, or freshly opened washing soda? Why?

4. Why are soda crystals regarded as a compound rather than as a mixture of sodium carbonate and water?

5. How could you make caustic soda, using washing soda as the source of the sodium?

6. How is metallic sodium protected from the action of the air?

7. What changes are seen when a bit of sodium is left for a long time exposed to the air? Give equations for chemical changes and explain the physical changes involved.

8. In a hollow in a large rock near the ocean, some small cube-shaped crystals were found. What substance had probably crystallized there?

9. What substance studied in this chapter might be used to dry gases?

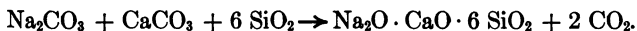
10. Why is sodium carbonate used to scrub dirty floors? Why is sodium hydroxide not used instead?

11. Why is sodium bicarbonate to be preferred to sodium carbonate for use in fire extinguishers?

12. What weight of metallic aluminium could be prepared by using 1 kilogram of sodium according to the reaction:



13. Glass is made by melting together sodium carbonate, limestone, CaCO_3 , and pure sand, SiO_2 , the reaction being approximately



What weights of materials would be taken to make 1000 kilograms of glass?

14. How many cubic meters of carbon dioxide would escape from the melting pot in Question 13?

CHAPTER XVIII

CALCIUM

SODIUM and potassium in the uncombined or metallic state are unfamiliar in everyday life, but in their compounds these elements are abundant and necessary to the welfare of mankind. Calcium is a metal that is like sodium and potassium in these respects as well as in many others. It is never found uncombined in nature, and in the metallic form it is not much more than a laboratory curiosity.

Calcium salts are found in sea water in very small quantity; they are found, too, in appreciable although small quantities in spring and river waters, especially those that are known as *hard* waters. Calcium is an even more abundant constituent of the rocks of the earth's surface than sodium or potassium. Limestone and marble, which are both calcium carbonate, CaCO_3 , gypsum, which is hydrated calcium sulphate, $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$, and phosphate rock, which is mainly calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$ are our most important natural compounds of calcium.

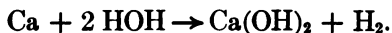
202. Preparation of Calcium. Metallic calcium can be obtained in much the same manner as metallic sodium. The electric current is passed through molten calcium chloride, which melts more easily than sodium chloride, and the metal is set free at the negative pole while the chlorine as usual is liberated at the positive pole.

203. Physical Properties. Metallic calcium is silver-white, and like all metals it has a metallic luster and conducts

electricity. It is harder, heavier, and tougher than sodium. It is about as hard as zinc; it is about one and one half times as heavy as water and thus it is light in comparison with iron, zinc, or copper; it is somewhat malleable and extremely tough.

204. Chemical Properties. Calcium is less active than sodium or potassium, but it is still an extremely active metal. This accounts for its never being found free in nature. Calcium is not much attacked by dry air at the ordinary temperature; in moist air, however, it is attacked quite rapidly. When heated, it catches fire and burns with intense heat, forming, in the main, the oxide CaO , but there is always a little nitride formed as well. When heated in pure nitrogen, calcium forms the nitride very readily. This nitride, however, will catch fire when heated in air and burn to the oxide.

Calcium reacts with cold water and liberates hydrogen:



This reaction is far less violent than the similar action of sodium, which, of course, is to be expected if calcium is a less active metal than sodium. Furthermore, calcium hydroxide is rather insoluble and is inclined to adhere to the metal surface, thus impeding the reaction with the water. Like sodium, calcium combines with all the non-metallic elements, but with considerably less violence in each case.

COMPOUNDS OF CALCIUM

205. Calcium Chloride, CaCl_2 , is an extremely soluble substance. It is left in solution in the carbon dioxide generator in which hydrochloric acid acts on calcium carbonate. Calcium chloride is not found extensively in nature. A very small amount is found in sea water; but large quantities

of it are obtained in chemical factories as by-products, just as it is left as a by-product in the generation of carbon dioxide. One of the chief uses of calcium chloride is in non-freezing solutions. It is, as stated, extremely soluble in water and a concentrated solution of it freezes at a temperature far below the freezing point of pure water. Hence calcium chloride solution is much used as a liquid to circulate in the cooling pipes of refrigerating plants.

206. Deliquescence. Calcium chloride is not only very soluble in water but it has a strong attraction for water. To illustrate this point, leave a few small lumps of calcium chloride exposed to the air on a watch glass. Soon the lumps are seen to be growing moist, and before long they have liquefied

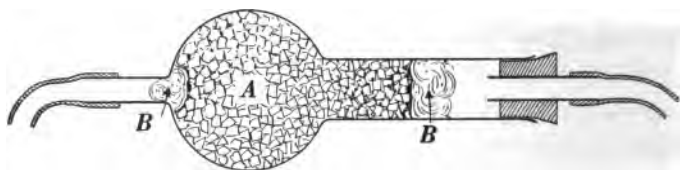


FIG. 36. — Calcium Chloride Drying Tube.

altogether. They have absorbed water vapor from the air and dissolved in the water so condensed. Such action is called *deliquescence*. This property suggests an important laboratory use for calcium chloride, namely, to dry gases. Some of this substance in granulated form (A) is placed in the center of a wide tube (drying tube) between two plugs of cotton (B) to keep it in place (Fig. 36). The gas to be dried, for example the hydrogen generated by the action of zinc on hydrochloric acid solution, and consequently nearly saturated with water vapor, is passed through this tube of calcium chloride and emerges practically free of water vapor.

207. Calcium Carbonate, CaCO_3 . This substance is found in nature in rocks of widely differing appearance. Iceland spar is the purest form. This is crystalline and as transparent as glass.

Marble is a very pure form, and it is beautifully white in consequence of its being composed of a mass of tiny crystals cemented together. The mass of crystals presents a dazzling white appearance for the



FIG. 37. — Iceland Spar.

same reason that snow does, snow consisting of a lot of tiny ice crystals. A compact block of ice is colorless and transparent like Iceland spar.

Limestone is the most abundant, although the least attractive, form of calcium carbonate. It shows less marked crystalline structure than marble, and it is usually of a dirty gray color.

The origin of limestone from the shells of sea animals of a previous age has been discussed under the subject of carbon dioxide. Limestone serves as the chief source of calcium compounds as well as an important source of carbon dioxide, for when it is heated, oxide of calcium is left as a solid, while the carbon dioxide escapes :



208. Calcium Oxide, or Quicklime, CaO . The decomposition of calcium carbonate by heat may be shown on a small scale if a little powdered marble is heated in a crucible in a Bunsen flame. That carbon dioxide is given off may be shown by introducing a drop of limewater suspended on a glass rod into the crucible. This is at once clouded and much more strongly than it would be by the gases coming from the flame alone. It is clouded but slowly when held in the same way in an empty crucible which is heated over a similar flame.

The residue is still a powder, but it no longer shows the glint of the crystal grains of the marble; it has a uniformly dull appearance. That it is different chemically from the original marble may be shown by barely wetting it with a few drops of water. If one observes carefully, it is noticed that considerable heat is produced. The effect may be better observed if a large lump of quicklime, that is, the commercial calcium oxide obtained by heating limestone in kilns, is dipped into water and then taken out. The lime is porous, and soaks up a good deal of water. Soon it is noticed that the lump is growing warm and a little later clouds of steam issue and the lump cracks and expands and finally falls to a fluffy white powder.

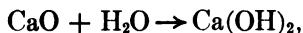
If some of this powder, or the powder left in the crucible, is wet with a little more water and placed on a piece of litmus paper, it colors the latter blue. This shows that the substance is alkaline. Now marble does not interact at all with water, and it has not the property of turning litmus blue.

The burning of limestone to make quicklime is an enormous industry, and rows of lime kilns are a familiar sight in the regions of limestone quarries. Large lumps of limestone are packed in the kilns, where they are heated for a number of hours either by being mixed with the burning fuel or,

better, by being subjected to the heat of the hot gases from the fire. The product is the quicklime of commerce. It is usually packed in barrels for shipment, but it is very important that the barrels be kept dry. If the lime gets wet, not only is its usefulness impaired but there is grave danger of fire, for the reaction with water may develop heat enough to set the wood of the barrel on fire.

Calcium oxide is very infusible, and thus lime finds a use in making crucibles and in lining furnaces for very high temperature work. Its use in the so-called limelight is particularly interesting. Here the flame of an oxy-hydrogen blowpipe is directed upon a block of lime which becomes intensely hot without melting and thus emits a brilliant white light.

209. Calcium Hydroxide, or Slaked Lime, $\text{Ca}(\text{OH})_2$. The reaction of quicklime with water,



yields calcium hydroxide, which is ordinarily known as slaked

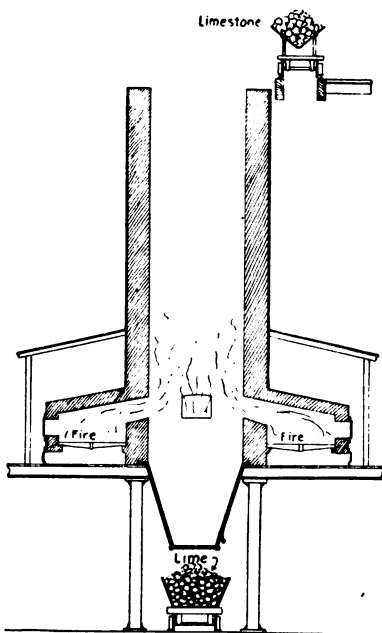
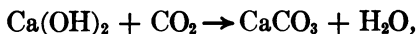


FIG. 38.—A Lime Kiln. The vertical shaft is packed with broken limestone. At regular intervals, the charge is replenished with fresh limestone at the top, as the quicklime is taken out from the bottom.

lime. Calcium hydroxide is slightly soluble in water, and as we have seen, the solution colors litmus blue, showing that it is alkaline. When slaked lime is stirred with water a saturated solution of calcium hydroxide is obtained, and if then the undissolved substance is allowed to settle, the clear solution may be siphoned off. This is known as *limewater*. Limewater is very useful on account of its mild alkalinity, and it is frequently mixed with the food of infants and invalids to counteract a sour or acid condition of the stomach. The use of limewater in testing for carbon dioxide has already been mentioned.

When slaked lime is agitated with water, only a little of the calcium hydroxide actually dissolves; the rest, which is very light and flocculent, becomes suspended in the liquid. Such a suspension is known as milk of lime because it has the appearance of milk. Common whitewash is nothing more than milk of lime.

Slaked lime finds, perhaps, its largest application in making mortar and plaster. Lime is mixed with enough water to slake it and leave it as a thin paste. Sand is then put in to give it body, and often hair is added in order to sustain the weight of the plaster until it hardens. After the plastic mass has been put in place with a trowel, it soon sets or hardens and makes a permanent part of the masonry or of the plastering of houses. The setting is due first to the drying out of the surplus water of the mixture, but the permanent setting is largely caused by a chemical reaction with the carbon dioxide of the air,



by which calcium carbonate is formed. Thus the plaster finally becomes chemically the same substance as the lime-

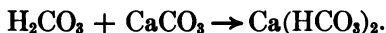
stone from which it was originally derived. In consequence of the small amount of carbon dioxide in the air and the slowness with which it can penetrate the mass of the plaster, the change from calcium hydroxide to calcium carbonate is almost never complete, the internal portions of the plaster remaining unchanged for many years. The water that is liberated during the setting of plaster is largely responsible for the dampness of the air in new buildings. Sometimes the setting of plaster is hastened by burning wood in stoves in new houses; the heat serves to help circulate the air and thus to more rapidly dry out the plaster, and the carbon dioxide from the fire, if allowed to escape into the air of the building, hastens the change of the slaked lime into calcium carbonate.

210. Water-slaked and Air-slaked Lime. Unless lime is preserved in hermetically sealed containers, a thing which it is practically impossible to do, lime must be used before it has stood too long because it is all the time deteriorating through action with the components of the air. In the first place, it reacts with the water vapor and slowly forms calcium hydroxide; then the calcium hydroxide reacts with the carbon dioxide and ultimately changes to calcium carbonate. Lime which has thus been kept too long has become *air slaked*. It then refuses to slake properly with water; that is, it fails to heat up strongly and fall to the powdery calcium hydroxide that we know as water-slaked lime.

211. Calcium Bicarbonate. A very interesting experiment which shows an important property of calcium bicarbonate is to blow the breath from the lungs through a glass tube into a test tube of limewater. As already seen (page 52), a turbidity is quickly produced, due to a precipitate of calcium carbonate formed from the carbon dioxide of the

breath and the calcium hydroxide of the limewater. But on persistently blowing the breath into the limewater, a surprising thing occurs; the turbidity disappears and we again obtain a clear solution.

This result is due to the formation of calcium bicarbonate, $\text{Ca}(\text{HCO}_3)_2$, a substance which is more soluble than calcium carbonate. After the calcium carbonate has all precipitated, the excess of carbon dioxide forms a weak solution of carbonic acid, and this reacts with the calcium carbonate:



An effect that is often seen on the marble shelves of soda fountains may be accounted for in the same way; namely,

where the carbonated water drips upon the marble a hollow is in time eaten away, due to the solvent action of the carbonic acid and the formation of calcium bicarbonate.

A similar phenomenon occurs in limestone regions in the earth. Water which percolates through the surface soil in wooded regions becomes nearly saturated with car-



FIG. 39.—Stalactites and Stalagmites in Mammoth Cave.

bon dioxide from the decaying vegetation; and when it flows through limestone, it slowly dissolves away the rock. Thus in the course of ages immense caverns are sometimes hollowed out. The famous Mammoth Cave of Kentucky is supposed to have been formed in this way.

212. Calcium Sulphate. This salt of calcium occurs in nature in the hydrated form as the mineral gypsum, $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$. Alabaster, which is used for fine vases and other ornamental purposes, is one of the natural forms of hydrated calcium sulphate. Calcium sulphate is also present in hard waters and in sea water, although it is but sparingly soluble. Plaster of Paris is made by partially dehydrating gypsum.

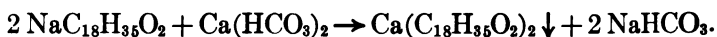


The reverse reaction takes place when the plaster is mixed with water and "setting" of the plaster results. The setting of cement, although much more complicated chemically than the setting of plaster of Paris, consists in the main in a similar addition of water to the finely powdered anhydrous material.

213. Hard Water. Water which contains calcium bicarbonate, or calcium sulphate, or in fact any soluble salt of calcium or magnesium, is said to be *hard*. Such water does not readily yield lather with soap, and if it is used in steam boilers, a deposit of mineral matter known as boiler scale is formed inside of the tubes to the great injury of the boilers.

214. Softening Hard Water. There are a good many kinds of soap, but for the purpose of discussing its action with hard water, we may regard soap as consisting of sodium stearate, $\text{NaC}_{18}\text{H}_{35}\text{O}_2$. Now sodium stearate is soluble in water, but calcium and magnesium stearates are not soluble. Therefore when soap is used with hard

water a precipitate of calcium or magnesium stearate is thrown down :



Any one who has tried to wash his hands with hard water and soap knows of the dirty sediment which collects in the wash basin.

Of course the amount of calcium and magnesium compounds in hard water is limited, and enough soap can be taken to react with all the hardness. After this, any addi-

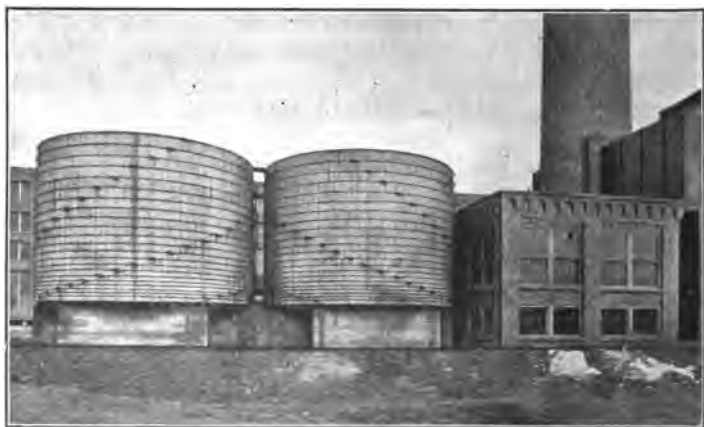


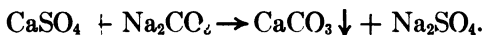
FIG. 40. — Settling Tanks, Water Softening Process.

tional soap forms lather freely. In laundries where a great deal of water is used, it would become a matter of considerable expense to depend upon soap to soften the water in this way.

It becomes necessary, therefore, to soften hard waters before they can be used in laundries or in steam boilers. If, as is very often the case, the hardness is caused by calcium bicarbonate alone, the method of softening is comparatively

simple. Calcium bicarbonate is very unstable, and is entirely broken up at the boiling temperature of water: $\text{Ca}(\text{HCO}_3)_2 \rightarrow \text{CaCO}_3 \downarrow + \text{H}_2\text{O} + \text{CO}_2 \uparrow$. So if the water is first heated, all of the calcium will be thrown down as insoluble calcium carbonate, and the water, which is now soft, may be used in the laundries or pumped into steam boilers. Hardness caused by calcium bicarbonate is known as *temporary hardness* because it can be so easily overcome by heating.

Permanent hardness can be remedied by adding chemical reagents which will precipitate the calcium and magnesium compounds. For example, if the hardness is caused by calcium sulphate, the addition of sodium carbonate will precipitate calcium carbonate, and leave the soluble but harmless sodium sulphate in solution:



This method is largely used in practice.

Either type of hardness can be removed by distillation, the involatile mineral substances remaining behind when the water evaporates. This last method, however, is too costly for extensive use, and is only employed when limited amounts of very pure water are necessary.

215. Valence. The pupil has doubtless wondered why the formula of sodium chloride is written NaCl and that of calcium chloride CaCl_2 ; that of water H_2O and that of hydrogen chloride HCl . Formulas, as we learned in Chapter XV, are used not only to designate substances, but to show their composition. The above formulas tell us, then, that one atom of sodium is combined with a single atom of chlorine, whereas one atom of calcium is combined with two atoms of chlorine; that an atom of oxygen is combined with two

atoms of hydrogen, whereas an atom of chlorine is combined with but a single atom of hydrogen.

Clearly the number of atoms of another element that one atom of a given element holds in combination is a very important property; this property has been given the name of *valence*. The valence of hydrogen in its compounds has been chosen as one for a standard of valence. The valence of chlorine in hydrogen chloride is one because one atom of chlorine is combined with a single atom of hydrogen. The valence of oxygen in water is two because the atom of oxygen is combined with two atoms of hydrogen. The valence of sodium in sodium chloride is one because one atom of sodium is combined with the same amount of chlorine that can combine with one atom of hydrogen. The valence of calcium in calcium chloride is two because an atom of calcium is combined with the same number of atoms of chlorine that can combine with two atoms of hydrogen.

It is to be noted that valence is concerned solely with the number of atoms that an atom of a given element holds in combination. It has nothing whatever to do with whether the other elements are held tenaciously or feebly.

SUMMARY

Calcium resembles sodium and potassium in many respects. It is never found in nature as the uncombined metal, but its compounds are very abundant and useful to mankind. The metal may be obtained by electrolyzing melted calcium chloride.

Properties of Calcium. Calcium is a very active metallic element, but it is less active than sodium or potassium. It combines with vigor with all non-metals. It displaces hydrogen from water, although not as vigorously as sodium or potassium. Metallic calcium is about as hard as zinc. It is heavier than sodium, but lighter than most metals. It possesses metallic luster and conducts electricity.

Important compounds of calcium are calcium carbonate, CaCO_3 , of which some of the rock of the earth's surface consists; calcium oxide or quicklime, CaO , which is obtained by strongly heating calcium carbonate; calcium hydroxide or slaked lime, Ca(OH)_2 , which is obtained by the action of calcium oxide with water.

Quicklime is used for making slaked lime in the preparation of mortar and plaster. The permanent hardening of these materials depends upon their combining with the carbon dioxide in the air, thus forming calcium carbonate.

Calcium carbonate reacts with carbonic acid to form calcium bicarbonate, which is somewhat soluble. In nature, water containing carbonic acid slowly dissolves limestone rock and forms caverns.

Calcium sulphate in a hydrated form occurs in nature as gypsum. Plaster of Paris is made by partially dehydrating gypsum.

Hard Waters. Water containing calcium bicarbonate or other soluble calcium or magnesium salts is known as hard water, and it cannot be satisfactorily used in laundries or in steam boilers. Temporary hardness, which is caused by calcium bicarbonate alone, may be remedied by pre-heating. Permanent hardness can be relieved by chemical treatment or by distillation.

The valence of an element is a property which depends on the number of atoms of another element which its own atom may hold in combination. The valence of calcium in its compounds is two.

Questions

1. Why cannot metallic calcium exist free in nature?
2. What occurs when marble is strongly heated?
3. How may limewater be prepared, starting with marble?
4. Why does a wood fire in a new house aid the setting of the plaster?
5. Explain the chemistry of limestone cave formation.
6. Can you offer an explanation of the formation of stalactites (consult a dictionary, if you are not familiar with the meaning of the word) in a limestone cave?

7. How might one soften a little hard water in order to obtain a good lather with soap?

8. What would be a good way to keep metallic calcium from oxidizing?

9. Mention two ways in which sea water might be softened for use in the boilers of a battleship. Which method would give the better drinking water?

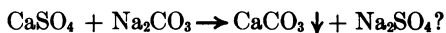
10. What marked difference of behavior on exposure to air might be used to tell whether a certain white solid was sodium carbonate or calcium chloride?

11. A crystal of gypsum (from which plaster of Paris is made) was heated moderately in a dry test tube. The upper walls of the tube became covered with moisture. The gypsum was dry when first heated. Explain.

12. What weight of water would be necessary to slake one kilogram of quicklime?

13. What volume of carbon dioxide must be absorbed by one kilogram of quicklime before it is completely air-slaked? What will be the final weight of the air-slaked lime?

14. Some hard water contains 0.5 gram of calcium sulphate per liter. How much sodium carbonate should be added to 1000 liters of the water to soften it according to the reaction:



15. If the same water were used for washing, what weight of soap would be used up by each liter of the water before a lather could be produced? (See Sec. 214, and use an equation similar to that there given.)

16. Starting on the basis of the valence of hydrogen as one, what is the valence of each of the elements in the following compounds:

HCl, HBr, H₂S, NH₃, CH₄;

H₂O, CaO, SnO₂, SO₃, OsO₄, Fe₂O₃, N₂O₅, Mn₂O₇;

HCl, AgCl, CuCl₂, FeCl₂, FeCl₃, SnCl₂, SnCl₄, PCl₃, PCl₅.

H₂O, CaO, CaS, Ca₃N₂.

CHAPTER XIX

ACIDS AND BASES; NEUTRALIZATION

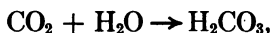
216. Properties of Acids. We have, up to this point, spoken of a few acids; namely, hydrochloric acid, sulphuric acid, and the very weak acid, carbonic acid, which is obtained when carbon dioxide dissolves in water. These acids, as well as other acids, have a good many properties in common, those properties that we have learned being, first, a sour taste, which is very strong with hydrochloric and sulphuric acids and much weaker with carbonic acid; second, ability to change the vegetable coloring matter litmus from blue to red; and third, ability to give off hydrogen gas when allowed to react with zinc, magnesium, or certain other active metals. Carbonic acid is weaker than the other acids, and one ordinarily fails to perceive any escape of hydrogen gas on treating this acid with zinc or magnesium.

217. Characteristic Component of Acids. The one constituent which is possessed by all acids is hydrogen, but it is hydrogen in a peculiar condition of combination, because this hydrogen is more or less easily displaced by metals. Water, alcohol, sugar, and petroleum all contain hydrogen, but these substances are not acids, for their hydrogen is not easily displaced by metals like zinc and iron, neither do these substances taste sour nor do they affect the color of litmus. The nature of this peculiar state in which hydrogen exists in acids will be taken up in a later chapter, and now we shall

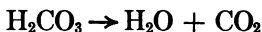
describe the manner in which a certain large class of acids — the so-called oxygen acids, or oxy-acids — is formed.

218. Oxy-acids; Carbon Dioxide and Carbonic Acid.

As we have seen, carbon burns in air or oxygen to form carbon dioxide, CO_2 , and the carbon dioxide dissolves to some extent in water, forming the weak acid, carbonic acid. It is believed that carbonic acid is a definite chemical compound formed from a molecule each of carbon dioxide and water:



but this compound, H_2CO_3 , is so feebly joined together — or to use the technical expression, it is so unstable — that it can only exist when dissolved in a comparatively large amount of water. As we know, when the pressure is released by removing the cork from a bottle of carbonated water, bubbles of a gas, which is carbon dioxide, commence to escape. The compound, carbonic acid, is breaking down, and the reaction



is taking place; that is, the reaction of formation is proceeding in the reverse direction.

219. Sulphur Dioxide and Sulphurous Acid. When sulphur burns, a very choking gas is formed, which is sulphur dioxide, SO_2 . This gas dissolves in water much more easily than carbon dioxide, and a more strongly acid solution is produced. The definite compound, sulphurous acid, H_2SO_3 , is supposed to be formed

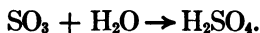


and to exist in the solution, but, like carbonic acid, it is unstable and readily breaks down again



except when it is dissolved in a large amount of water. Under ordinary pressure and at 20° C. one volume of water will dissolve nearly 40 volumes of sulphur dioxide. The solution so formed is far more strongly acid than that of carbon dioxide, and it smells strongly of sulphur dioxide on account of the continuous slow escape of that gas.

220. Sulphur Trioxide and Sulphuric Acid. There is another oxide of sulphur, sulphur trioxide, SO_3 , which can be prepared if sulphur dioxide is allowed to combine with more oxygen under the right conditions. These conditions will be more fully discussed in the chapter on sulphur. Sulphur trioxide is extremely soluble in water, — in fact, this hardly expresses it; the sulphur trioxide has a great chemical affinity for water, as is evidenced by the large amount of heat developed when the two substances come in contact. Indeed, the greatest caution must be exercised in adding sulphur trioxide to water if one would avoid a dangerously violent reaction.



In this case, there is no doubt of the existence of the definite compound H_2SO_4 ; for unlike carbonic and sulphurous acids, it can be prepared pure. At a low temperature it can be obtained as a crystalline solid, but at ordinary temperatures it is a thick, oily liquid. It can be proved by chemical analysis to have the composition corresponding to the formula, H_2SO_4 . The pure substance does not show very marked acid properties, but it mixes freely with water and its fairly dilute solution is very strongly acid.

221. Phosphorus Pentoxide and Phosphoric Acid. When phosphorus burns with plenty of air, the oxide formed has the composition P_2O_5 . This oxide combines with the water as

vigorously as does sulphur trioxide. It forms with the water several clearly defined compounds, but the most important one is the common phosphoric acid, H_3PO_4 .



This compound can be prepared pure as a crystalline solid which melts at 37°C . (about the body temperature) to a sirupy liquid. Like pure sulphuric acid, this pure substance has no marked acid properties, but it mixes easily with water, and the dilute solution is distinctly acidic, — about as strongly acidic as the solution of sulphurous acid.

222. Non-metals are Acid-forming Elements. We have now seen that the oxides of three different elements, carbon, sulphur, and phosphorus, can combine with hydrogen oxide, or water, to form compounds,



and that these compounds, when dissolved in or mixed with large additional amounts of water, show acid properties.

The three elements just mentioned are non-metals. It is one of the important chemical properties of non-metallic elements that their oxides are *acid-forming*. Non-metallic elements possess distinct physical as well as distinct chemical properties; for they are poor conductors of heat and electricity, and they do not usually possess a metallic luster. Metals can be easily distinguished by their peculiar metallic luster and by the ease with which they conduct heat and electricity.

The non-metallic oxides from which acids can be formed

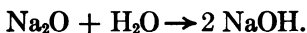
by combination with water are known as *acid anhydrides*, the term anhydride being derived from Greek words meaning *without water*.

As we know, hydrogen is essential in the make-up of an acid. The anhydride contains no hydrogen, but the water does, although in water this hydrogen is so closely bound to the oxygen that it is not readily displaced by metals like zinc or magnesium, nor does the hydrogen of water exhibit the other characteristics of acids, such as the sour taste and the power to redden litmus. When the acid anhydride is added to water, it seems to partially appropriate the oxygen of the water, leaving the hydrogen less closely bound. So the hydrogen becomes *displaceable* by metals, and at the same time it develops the properties of sour taste and effect on litmus. It is for this reason that in the formula of an acid the hydrogen is written by itself, and the group containing the acid anhydride plus the oxygen from the water is all written together: $\text{H}_2 \cdot \text{SO}_4$ instead of $\text{H}_2\text{O} \cdot \text{SO}_3$.

223. Metals are Base-forming Elements. All elements belong to one of two classes, either to the metals or the non-metals. There is, however, no sharp boundary between these classes, but rather, there is a gradual transition, and some of the elements in between might at one time be classed as metals and at another as non-metals. We know that the physical properties of metals are very characteristic; the chemical properties are equally so. One of the most important of the chemical properties is the behavior of the oxides of the metals; for these, instead of forming acids like ~~the oxides of the non-metals~~, when they combine with water, produce *bases*, which are the exact opposites of acids.

224. Sodium Oxide and Sodium Hydroxide. When sodium burns with a plentiful supply of air, sodium peroxide,

Na_2O_2 , is formed. This substance has already been mentioned as a source of hydrogen peroxide and of oxygen. But in the present connection we are more interested in sodium oxide,¹ Na_2O , which can be prepared by burning sodium with a limited amount of oxygen. This oxide of sodium reacts very vigorously with water, producing great heat, just as sulphur trioxide and water produce great heat; and a distinct new substance — sodium hydroxide — is formed:



Sodium hydroxide is a solid white substance. It will dissolve in less than its own weight of water. Its solution possesses properties which are almost the exact opposite of the properties of acid solutions. It has an alkaline instead of a sour taste; in experimenting to find out what this taste is, only very dilute solutions should be used, — not more than one part by weight of sodium hydroxide to 1000 parts of water; it turns red litmus *blue*, and it has the power of neutralizing acids.

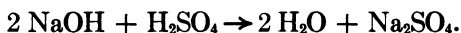
These *alkaline* properties are characteristic not only of a sodium hydroxide solution, but of the solution of any soluble base. A base is obtained when a metallic oxide combines with water, and sodium hydroxide is one of the strongest bases.

225. Neutralization. When a solution of sodium hydroxide is added little by little to a solution of any acid, — let us say sulphuric acid, so as to have a concrete example, — it is found that the acid properties grow less and less marked until at a certain point they disappear altogether; addition

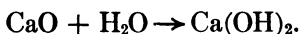
¹ This is sometimes called sodium *monoxide* when it is wished to distinguish it from the peroxide. Otherwise, sodium oxide always means this oxide.

of any further sodium hydroxide imparts the characteristics of a base to the whole solution. At the exact point at which the acid properties have disappeared and the basic properties have not begun to appear the solution is *neutral*, just as pure water is neutral. The process of just destroying acid properties by the careful addition of a base is known as *neutralization*; likewise the reverse process, that of exactly removing all basic properties by carefully adding an acid, is neutralization.

In the above process of neutralization exactly two moles of sodium hydroxide must be added to destroy the acid properties of each mole of sulphuric acid, or, in other words, one molecule of sodium hydroxide for each acid hydrogen in a molecule of sulphuric acid. If the neutralized solution is evaporated, it is found that after all the water is driven off a solid white substance is left, which is sodium sulphate. The reaction of neutralization may be formulated:



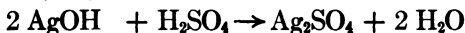
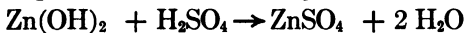
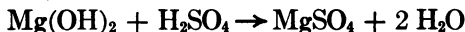
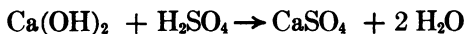
226. Calcium Oxide and Calcium Hydroxide. The metal calcium yields calcium oxide on burning. Calcium oxide is the very common substance that is known as quicklime, and it is, of course, usually obtained by a cheaper method than that of burning the rather expensive metallic calcium. Treated with water, calcium oxide shows characteristics similar to those of sodium oxide; for a great deal of heat is produced and a base is formed, according to the reaction:



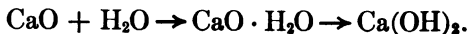
As we have seen in the preceding chapter, the saturated solution of calcium hydroxide, which is known as limewater, possesses the same alkaline properties as sodium hydroxide solution, but to a smaller degree, because calcium hydroxide

is so insoluble that the solution contains a comparatively small amount of the base.

227. Other Basic Oxides and Bases. Oxides of other metals can yield bases; as, for example, magnesium oxide, $\text{MgO} + \text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})_2$; zinc oxide, $\text{ZnO} + \text{H}_2\text{O} \rightarrow \text{Zn}(\text{OH})_2$; silver oxide, $\text{Ag}_2\text{O} + \text{H}_2\text{O} \rightarrow 2 \text{AgOH}$; but these last-mentioned bases are much weaker in their basic properties than sodium or calcium hydroxide. All of these bases are capable of neutralizing acids as shown in the following reactions:



228. Characteristic Component of Bases. It has already been seen that the displaceable hydrogen of acids is the component responsible for the acid characteristics. When this component is removed during neutralization, the acid properties disappear. It is evident from the above reactions that bases likewise have a certain component which must be responsible for the basic properties, and this component is the OH, or hydroxyl group. As the non-metallic oxide is known as an acid anhydride, so the metallic oxide from which a base is formed by combination with water is known as a *basic anhydride*. It is evident that the hydroxyl group cannot have come wholly from the basic anhydride. It appears as if the basic anhydride had attached to itself a molecule of water, $\text{CaO} + \text{H}_2\text{O} \rightarrow \text{CaO} \cdot \text{H}_2\text{O}$ and that this compound had rearranged itself so that its hydrogen and oxygen formed two hydroxyl groups



229. Formation of Water in Neutralization. In the process of neutralization it is the hydrogen of acids and the hydroxyl of bases which mutually destroy each other's properties. They simply combine to form water

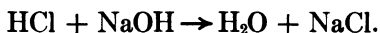


in which, as we know, neither basic nor acidic properties are manifest. It would appear as if in water these components were very closely bound together, whereas the hydrogen of acids and the hydroxyl of bases are less closely joined to the rest of the molecule and are thus free to manifest their specific properties.

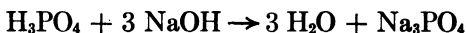
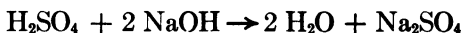
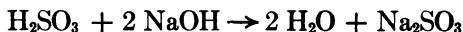
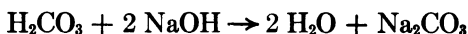
230. Formation of Salts during Neutralization. The formation of water during neutralization accounts for two of the original components of the acid and base. The other components, that is, the metal of the base and the radical of the acid, constitute a salt which in many cases remains dissolved in the solution; in other cases in which the particular salt is insoluble it separates out at once as a solid precipitate. In any case, solid salt may be made to separate out if the water — both the original solvent water and the water produced in the neutralization — is evaporated off by heat. The immediate and invariable product of every neutralization is water, but besides this there is always a salt which is different for every different acid and base. A salt may be defined as a substance which is composed of the metal of some base and the radical of some acid. Different salts differ, of course, in many respects among themselves, but we shall find that salts, as a class, have a good many properties in common.

231. Acids containing no Oxygen. We have just seen that acids and bases may be formed by the union of non-

metallic oxides and metallic oxides, respectively, with water. But there are acids and bases other than those formed in this way. We have seen that the essential component of an acid is displaceable hydrogen, and the essential component of a base is a loosely attached hydroxyl group. Hydrogen chloride, a compound already familiar to us, contains only hydrogen and chlorine, yet when it is dissolved in water, its hydrogen assumes the easily displaceable condition that is characteristic of an acid. Hydrochloric acid is one of the strongest acids. It neutralizes bases in just the same manner as all other acids; for example, it reacts with sodium hydroxide, giving water and sodium chloride:

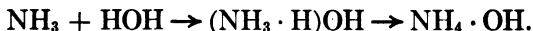


232. Acid Radicals. When the neutralization reactions of the oxy-acids are compared with that of hydrochloric acid,

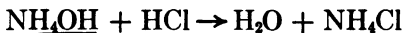


it becomes obvious that the groups CO_3 , SO_3 , SO_4 , and PO_4 function in the same manner as the single atom Cl ; that is to say, these groups remain intact while the hydrogen is removed and the metallic element takes its place. The term radical is used to denote this part of an acid which remains unchanged when the acid is neutralized, and the radical may consist of a single element only; as, for example, chlorine, or of several elements. Salts, of course, contain the same radicals as the acids from which the salts are derived.

233. Ammonium Hydroxide. We have not yet discussed ammonia; ammonia water, however, is something familiar to every one. It is used in the household for cleansing purposes because it is a mild alkali. Ammonia itself is a gas containing only hydrogen and nitrogen, and its formula is NH_3 . It is thus in no respect a metal oxide, yet it dissolves freely in water and gives a solution that shows the characteristics of a base. This indicates that in some way the water has been altered so that loosely bound hydroxyl groups now exist. The NH_3 molecules may be supposed to have each appropriated one of the H atoms of a water molecule to form the group NH_4 , which is known as the ammonium group, or radical, whereby the OH of water is left in the loosely bound condition:



234. Metallic Radicals. Ammonium hydroxide can be used to neutralize an acid,



and it is found that the ammonium group remains intact during the process and that it enters into the composition of the salt, ammonium chloride. A group like this, which plays the same part in a base or salt as the atoms of single metallic elements, is likewise known as a radical, — a metallic radical, in this case.

Every one knows that ammonia water is not nearly so caustic an alkali as sodium hydroxide. Ammonium hydroxide is, as a matter of fact, a much weaker base. The cause of greater or less strength among the different bases and acids has not yet been suggested, but it is to be discussed in Chapter XXV.

SUMMARY

Acids contain hydrogen and a radical consisting of a non-metal or of non-metallic elements. When the acid is dissolved in water, the attachment between the hydrogen and the radical is apparently weakened, so that the hydrogen is displaceable by metals, and is free enough to manifest its characteristics of sour taste, power to redden litmus, and ability to combine with the hydroxyl of bases, thereby neutralizing the latter.

The oxides of the non-metallic elements form acids when combined with water.

Bases contain the hydroxyl group, OH, and a metallic element or radical. When a base is dissolved in water, the hydroxyl group becomes active, in the same manner as the hydrogen of acids. It then displays its characteristics of alkaline taste, power to turn litmus blue, and ability to neutralize acids.

The oxides of the metallic elements form bases when combined with water.

When an acid and base neutralize each other, the hydrogen of the one and the hydroxyl of the other combine to form water and thus disappear as active components, while the metal or metallic radical of the base and the non-metallic radical of the acid together yield a salt.

Questions

1. Cream of tartar has a sour taste. This taste is due to the presence of what component in the cream of tartar?

2. To the presence of what group of elements would you attribute the alkaline taste of limewater (calcium hydroxide solution)?

3. What becomes of the components which are responsible for the sour taste and the alkaline taste, respectively, when an acid is neutralized by a base?

4. What is a salt? What acid and what base yield common salt by neutralization?

5. How could you make sodium sulphate from (a) sodium hydroxide? (b) sodium chloride? (c) sodium carbonate? Give equations.

6. If one has spilled sulphuric acid on his garment, why does he use ammonia water to prevent a hole being eaten? Why not use sodium hydroxide?

7. Why does limewater correct sour stomach?

8. What weight of (a) hydrochloric acid, (b) sulphuric acid, should be taken to neutralize 40 grams of sodium hydroxide?

9. What volume of carbon dioxide (standard conditions) should be passed into a solution of 40 grams of sodium hydroxide to form sodium carbonate — $2 \text{NaOH} + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$?

10. Ammonium salts are obtained from the liquors condensed in gas works by distilling off ammonia and passing it into acid. What volume of ammonia gas (standard conditions) can be caught in one kilogram of sulphuric acid?

11. What volume of potassium hydroxide solution containing 100 grams KOH per liter will just neutralize 100 c.c. of hydrochloric acid containing 200 grams HCl per liter?

12. Cite several examples in which an acid is made by treating the oxide of a non-metal with water; in which a base is made by treating the oxide of a metal with water.

CHAPTER XX

NOMENCLATURE.

SEVERAL acids, bases, and salts have been discussed in the last chapter, and names have been used for them which are probably not as yet fully understood by the pupil. It seems best, therefore, to pause at this point and explain the system of naming which is in use generally by chemists.

235. As has already been explained, when a substance consists of but two elements, its name includes the names, or at least the roots of the names, of each element, the more metallic element being taken first, and the suffix *ide* is added to the name of the second element. The suffix *ide* has this significance; namely, it indicates a compound consisting usually of only two elements:

HCl	hydrogen chloride
NaCl	sodium chloride
H ₂ O	hydrogen oxide
Na ₂ O	sodium oxide
H ₂ S	hydrogen sulphide
Na ₂ S	sodium sulphide.

236. It frequently happens that two elements form more than one compound with each other (see law of Multiple Proportions). One method of distinguishing the different compounds in such a series is by using the Greek or Latin prefixes before the name of the non-metal in order to indicate the number of atoms of this element.

CO	carbon monoxide
CO ₂	carbon dioxide
SO ₃	sulphur trioxide
CCl ₄	carbon tetrachloride
PCl ₅	phosphorus pentachloride.

237. When a compound of two elements is an acid and it is wished to indicate this fact, the word *acid* is added to the name, and the names of the two elements are contracted into a single word which is now used as an adjective with the common English adjective ending *ic* instead of *ide*.

HCl	hydrochloric acid
H ₂ S	hydrosulphuric acid
HBr	hydrobromic acid.

On passing from the simpler acids containing only two elements to the more complicated oxy-acids which contain three elements, the naming becomes simpler instead of more complicated. It must be remembered that the oxy-acids were the first acids to be discovered; indeed, it was thought formerly that oxygen was the essential acid-producing constituent of acids. It is only comparatively recently that hydrogen has become recognized as the true acid-producing constituent. Acids were thus originally named, in accordance with this erroneous conception, after the non-metal whose oxide gave the acid when it united with water. For example, carbonic acid was the acid derived from the oxide of carbon. This nomenclature has proved perfectly satisfactory and has been retained.

The suffix *ic* is the common termination for the names of acids. Some of the non-metals have more than one oxide and, corresponding to the different oxides, yield more than one acid. In such cases the suffix *ic* is retained for the

commonest, or the most important, of these acids. For an acid containing less oxygen, the suffix *ous* is used (*ous* is another common English adjective ending).

Thus, the most important acid from sulphur is sulphuric acid, derived from sulphur trioxide. From sulphur dioxide an acid with less oxygen is obtained which is called sulphurous acid. The acid which contains hydrogen and sulphur alone is distinguished from these oxy-acids in that the prefix *hydro* is used.

OXIDE	FORMULA OF ACID	NAME OF ACID
—	H ₂ S	<i>Hydro sulphuric acid</i>
SO ₂	H ₂ SO ₃	<i>Sulphurous acid</i>
SO ₃	H ₂ SO ₄	<i>Sulphuric acid</i>
P ₂ O ₃	H ₃ PO ₃	<i>Phosphorous acid</i>
P ₂ O ₅	H ₃ PO ₄	<i>Phosphoric acid</i>

238. Some elements, notably chlorine, yield more than two acids. In such cases the prefix *per* is used to denote a greater oxygen content than that of the plain *ic* acid, and the prefix *hypo* to denote a lower oxygen content than that of the plain *ous* acid. To illustrate this point, the chlorine acids, including the acid with no oxygen, are given in the following table :

OXIDE	FORMULA OF ACID	NAME OF ACID
—	HCl	<i>hydro chloric acid</i>
Cl ₂ O	HClO	<i>hypo chlorous acid</i>
Cl ₂ O ₃	HClO ₂	<i>chlorous acid</i>
Cl ₂ O ₅	HClO ₃	<i>chloric acid</i>
Cl ₂ O ₇	HClO ₄	<i>per chloric acid</i>

239. Bases always consist of a metallic element combined with hydroxyl. In naming bases, the name of the metal is first given, and this is followed by the word hydroxide.

NaOH	sodium hydroxide
KOH	potassium hydroxide
Zn(OH) ₂	zinc hydroxide.

The termination *ide* usually signifies that a compound containing only two elements is indicated. Still its use in this case is justified on the ground that the OH group behaves quite like a single atom.

240. Salts may be derived by the neutralization of bases and acids and are named in accordance. Salts containing but two elements are named according to the rule already given for compounds of only two elements. Salts of oxyacids are named after the acids, except that the ending *ic* is changed to *ate* and the ending *ous* is changed to *ite*. The prefixes *hypo* and *per* are retained in the names of the oxy-salts, but the prefix *hydro* is not retained in the names of the salts derived from the *hydro*-acids.

FORMULA OF ACID	NAME OF ACID	FORMULA OF SODIUM SALT	NAME OF SALT
HCl	hydrochloric acid	NaCl	sodium chloride
HClO	hypochlorous acid	NaClO	sodium hypochlorite
HClO ₂	chlorous acid	NaClO ₂	sodium chlorite
HClO ₃	chloric acid	NaClO ₃	sodium chlorate
HClO ₄	perchloric acid	NaClO ₄	sodium perchlorate
H ₂ S	hydrosulphuric acid	Na ₂ S	sodium sulphide
H ₂ SO ₃	sulphurous acid	Na ₂ SO ₃	sodium sulphite
H ₂ SO ₄	sulphuric acid	Na ₂ SO ₄	sodium sulphate
HNO ₂	nitrous acid	NaNO ₂	sodium nitrite
HNO ₃	nitric acid	NaNO ₃	sodium nitrate

Questions

1. Name the compound whose formula is KI.
2. Name the acid from which KI is derived.
3. What acid yields iodates on neutralization?
4. What acid yields perchlorates?
5. Name the sodium salt of phosphorous acid.
6. Name the potassium salt of hypochlorous acid.
7. What acid yields hypochlorites?
8. Name salts derived from silicic acid.
9. Name compounds having the following formulas: NaBr, HBr, KBrO, $\text{Ca}(\text{BrO}_3)_2$, KIO_4 , H_2S , K_2S , CaSO_3 , KNO_2 , $\text{Zn}(\text{NO}_3)_2$.
10. Give the formulas of potassium chloride, potassium sulphide, potassium sulphite, ammonium sulphate, potassium perchlorate.

CHAPTER XXI

THE METALS

It has already been seen that it is impossible to deal with the chemistry of the non-metals without describing the compounds that they form with the metals. We have already acquired some knowledge of the metals sodium and calcium and a fragmentary knowledge of some of the other metals; to make this knowledge more systematic, we shall devote this chapter to the study of the metals and the following chapter to the methods of winning the metals from the rocks and earths in which they are found in nature.

241. Physical Properties of Metals. A metal can be almost unerringly recognized even at a glance by its peculiar luster, — the so-called metallic luster. It is very difficult to describe metallic luster, but it is something that would never be confused with the luster of non-metallic substances such as glass, or sulphur crystals.

Besides having metallic luster, all metals have a high degree of conductivity for heat and electricity.¹

Many of the common metals are strong, or hard, or ductile, or tenacious, or malleable, or heavy, or difficult to melt, but none of these properties are distinctive of the metals,

¹ It is true that graphite (carbon) and some of the sulphides and oxides of the heavy metals, for example, magnetic oxide of iron, possess metallic luster and conduct electricity. They thus possess the distinctive physical properties of the uncombined metals, but this does not impair the correctness of the above statement that all metals have these properties.

as are the metallic luster and the conductivity for heat and electricity. For example, iron is strong, hard, and difficult to melt, but lead is weak, soft, and easily melted. Gold and copper are ductile and malleable, but chromium, manganese, and bismuth are so brittle that they can be broken into fragments with a hammer. Platinum will barely melt in the oxy-hydrogen blowpipe, while sodium will melt below the temperature of boiling water, and mercury melts at a temperature $40^{\circ}\text{C}.$ below the melting point of ice. Gold, lead, and mercury are very heavy; aluminium and magnesium are light, and sodium is so light, that it floats on water.

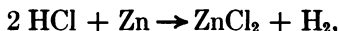
To sum up the physical characteristics of metals: the metallic luster and the conductivity for heat and electricity are properties possessed by the metals without exception. Numerous other properties are associated in the popular mind with metals, but they are not invariable and distinctive properties of metals.

242. Chemical Properties of Metals. In chemical properties the metals are as different from the non-metals as in physical properties. One of the most striking chemical characteristics of the metals has already been mentioned in Chapter XIX; namely, that the oxides of the metals are base-forming in distinction to the oxides of the non-metals, which are acid-forming.

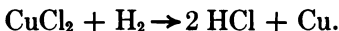
Acids and bases are opposed to each other in their chemical nature, as we may conclude from their ability to neutralize each other. In a similar way, the metals and the non-metals themselves are opposed to each other in their chemical nature, for they are capable of changing, or neutralizing, each other's properties when they combine. We are familiar, for example, with the striking properties of sodium and the striking properties of chlorine; when these elements com-

bine, these striking properties disappear and we have ordinary common salt, which does not have the metallic luster and the conductance for electricity of sodium nor the evil odor and the yellowish color of chlorine.

243. Hydrogen as a Metal. The element hydrogen does not possess the physical characteristics of metals, but in chemical properties it shows a strong resemblance to the metals. It combines with non-metals, forming such compounds as hydrogen chloride and water, but it does not show any marked tendency to form compounds with the metals. Furthermore, hydrogen is interchangeable with the metals in nearly all of their compounds. For example, on treating an acid such as hydrogen chloride with zinc or iron, the metals displace hydrogen according to the equations:



Zinc chloride and iron chloride, then, may be regarded as hydrochloric acid in which zinc or iron has been substituted for hydrogen. When copper chloride is heated in hydrogen gas, uncombined copper and hydrogen chloride are obtained:



Hydrogen chloride may be regarded as copper chloride in which hydrogen has been substituted for copper.

It is thus seen that metals, including hydrogen, all have the same kind of combining power. So, if one metal forms a chloride, then all of the metals including hydrogen should do the same. It is in fact true that all of the metallic elements form distinct chlorides. Nearly all likewise form oxides.

Not only are metals interchangeable with hydrogen in

the simple compounds hydrogen chloride and water, but also in the oxy-acids such as sulphuric, phosphoric, and carbonic acids, in which hydrogen is in combination with radicals instead of with single elements. In fact, sulphates, phosphates, and carbonates of all the most active metals are well known. Whole mountain ranges, for example, are composed of calcium carbonate and magnesium carbonate, and deposits of calcium sulphate and calcium phosphate, of iron carbonate, copper carbonate, zinc carbonate, and lead carbonate are often found in the earth.

244. Electrical Nature of Chemical Attraction. It is clear from what has already been said that it is oppositeness in chemical nature that makes it possible for two elements to form compounds. We know that when an electric current is passed through water, the latter is decomposed into hydrogen and oxygen; likewise hydrochloric acid is decomposed into hydrogen and chlorine. The hydrogen is liberated in each case at the negative electrode, and since it is known that unlike electric charges attract each other, whereas like charges repel, it must be that the hydrogen in the compound is electrically positive in order to be attracted to the negative electrode. According to the same reasoning, since the oxygen and chlorine are liberated at the positive electrode, these must be electrically negative as they exist in their compounds. Like hydrogen, the metals must all be electro-positive in their compounds; for they are always set free at the negative electrode when the current is passed through solutions of any of their salts.

We are certain that in many compounds the attractive force holding the elements together is in some way dependent on their electrical condition. It may be that this is true of all chemical compounds, although this would be too sweeping

a statement to make unconditionally in the light of our present knowledge.

At all events this statement may be made without reservation: that *in compounds of metals and non-metals the metals are electro-positive in nature and the non-metals are electro-negative.*

245. Compounds of Non-Metals with Non-Metals. — It is true that non-metals often form compounds among themselves; as, for example, in the oxides of carbon, sulphur, and phosphorus. There must be some difference in nature to make the chemical union possible, and if this difference is electrical, it must be that the carbon, sulphur, and phosphorus are forced to play the electro-positive rôle in these compounds because the oxygen has so much greater ability to play the electro-negative rôle. It is true, however, as a general rule that the compounds of the non-metals among themselves are feebler (that is, much more easily broken apart) than the compounds of the non-metals with the metals.

246. Compounds of Metals with Metals; Alloys. Metals show even less tendency to form compounds among themselves than do the non-metals. When different metals are melted and poured together, alloys are obtained: brass is an alloy of copper and zinc; bronze an alloy of copper and tin; solder an alloy of tin and lead. These alloys are not definite compounds of the metals, but are in the main mixtures, much like the mixture that we obtain by pouring alcohol and water together. The molten metals mix, and when the mixture cools, it solidifies to a metallic mass which has metallic luster and conducts electricity as do both of its component metals.

The most recent study of alloys has indeed proved that

they sometimes contain minute crystals of certain definite compounds embedded in the mass of the metal. These crystals can sometimes be observed with a microscope on a polished surface of the alloy that has been carefully etched with acid. At best, however, the power of metals to combine chemically with other metals is very limited.

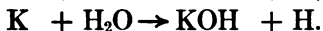
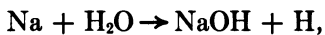
247. Classification of the Metals. Now that we have shown in a general way how metals are different from non-metals, let us divide them into groups or classes according to their properties. They might be classed according to their base-forming properties or according to their behavior with acids, or according to their physical properties. We shall group them into three main classes; namely, the alkali metals, the earth-forming metals, and the heavy metals. This grouping is in the main based on the physical property of weight, although the chemical properties also follow this grouping to a great extent.

248. The alkali metals are those from which the *caustic alkalies* are obtained. We have already considered the two of most frequent occurrence; namely, sodium and potassium, which yield the bases, sodium hydroxide and potassium hydroxide respectively. These bases are extremely soluble and their concentrated solutions are *caustic* or corrosive to the flesh or to any animal or vegetable tissues. The terms alkali and base are somewhat interchangeable. A base, as seen in Chapter XIX, is a substance that contains an hydroxyl group and can neutralize an acid. An alkali is a substance that dissolves freely in water and then shows to a marked degree the characteristics of soluble bases. For example, an alkali turns red litmus blue, it has an alkaline taste, it is useful in cleansing or removing grease and dirt.

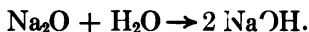
As already seen, metallic sodium and potassium are light

in weight, — they will float on water; they are soft and can be cut with a knife almost as easily as cheese; they melt below the boiling point of water. These metals conduct electricity and show a bright metallic luster on freshly exposed surfaces. Exposed to the air, the surfaces soon grow dull on account of the formation of a layer of oxide or hydroxide on the surface.

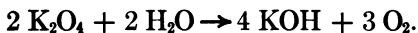
Sodium and potassium both react violently when thrown on cold water. They float around, giving a rapid evolution of hydrogen, and, especially with potassium, the heat of the reaction is so intense as to set fire to the hydrogen. The reaction yields the hydroxides:



Sodium and potassium combine violently with oxygen and chlorine when heated in these gases. The alkali metals are, in fact, the most active of the metallic elements. The oxides react energetically with water and give the hydroxides. For example, sodium oxide reacts as follows:



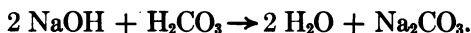
It has already been mentioned that when sodium burns in a plentiful supply of air, a higher oxide — a so-called *peroxide* — is formed. Potassium also forms a peroxide, K_2O_4 . When either of these peroxides is treated with water, the ordinary hydroxide is obtained just as from the monoxide, and the excess of oxygen escapes as oxygen gas:



Since the alkali metals are the most energetic of the metallic elements and show so great a tendency to react

with the abundant substances, water and oxygen, it is not strange that these metals are never found uncombined in nature. Nearly all the salts of the alkali metals are very soluble in water.

The most generally useful and important compounds of the alkali metals are the hydroxides and the carbonates. The hydroxides constitute the caustic alkalies, the carbonates are mild alkalies. We might expect that the carbonates would be neutral and not alkaline, because they are salts and may be obtained by neutralizing a base with an acid:



But it must not be lost sight of that sodium hydroxide is an extremely strong base, whereas carbonic acid is a very weak acid. This fact permits the neutralization to reverse itself to a certain extent when water has access to salts of this type and hence a little of the base is present in the solution (see Hydrolysis, p. 405).

249. Ammonium. The ammonium group, or radical (NH_4), as we have already seen in Chapter XIX, acts chemically very much like a metal. Its compounds are almost without exception soluble, as are those of the alkali metals, and like them, its hydroxide is very soluble in water and is a pronounced base (or alkali). Hence the hypothetical metal ammonium is classed among the alkali metals.

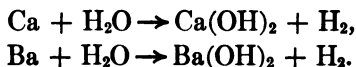
250. The Earth-forming Metals. Our next class of metals, the earth-forming metals, is, as the name implies, a group whose compounds form a large part of the earthy matter of which the surface of our earth is made. The most important metals in this class are magnesium, calcium, barium, and aluminium.

In physical properties these metals are much harder and

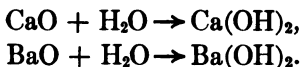
more tenacious than the alkali metals, although they fall a good deal below iron in these respects. They are light in weight as compared with the heavy metals iron, copper, and zinc, but they are heavier than the alkali metals. One of the very valuable properties of aluminium is its lightness, for it approaches iron in strength and yet it is of far less weight. These metals all have fairly high melting points.

The earth-forming metals are like the alkali metals in that they could by no possibility remain long uncombined in the earth, and as we should expect, they are always found in a state of combination.

Of the metals mentioned in this class calcium and barium are most like the alkali metals, for they react with cold water and liberate hydrogen :



Likewise, their oxides react energetically with water to form hydroxides :

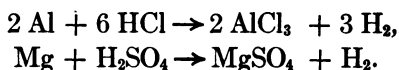


The hydroxides are not so soluble as the hydroxides of the alkali metals and are not so strongly basic. Calcium and barium are often called alkaline earth metals to show that they are intermediate between alkali metals and the more strictly earth metals.

Magnesium and aluminium do not react appreciably with cold water. Their hydroxides are bases and react with acids to form salts; magnesium hydroxide is almost insoluble, and aluminium hydroxide is still less soluble and withal a very weak base. Although these bases are insoluble

in water, they dissolve easily in dilute acid solutions because their salts, which are soluble, are formed.

All of the earth-forming metals react vigorously with acids with displacement of hydrogen and formation of the corresponding salt:



These metals are thus shown to be more active than hydrogen, as is also shown by the fact that it is impossible to reduce their oxides by heating them in hydrogen.

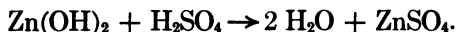
Magnesium and barium, like calcium, are found frequently in nature as the carbonates.

Aluminium is the most abundant of the metallic elements in the earth's crust. It occurs as silicate in clay and in most of the rocks of the earth's crust. Metallic aluminium is obtained almost solely by the electrolysis of the hydrated oxide which is found in the earth in fair abundance as the mineral bauxite.

251. The Heavy Metals. The remaining metals that we have to consider we shall group together under the title of the *heavy metals*. The most important ones of this group are copper, silver, gold, mercury, platinum, zinc, tin, lead, chromium, manganese, iron, and nickel, and it may be seen that this list includes all, except aluminium, of the metals that are familiar in our everyday life.

As the name implies, these metals are all of high specific gravity. They possess to a high degree the characteristic physical properties of metals; that is, metallic luster and conductivity for heat and electricity. Most of them have great strength and considerable hardness, which make them useful for structural purposes and for making machines and utensils.

In chemical properties the metallic character is not so strongly marked in this group as in the other two groups. The heavy metals form hydroxides which are capable of neutralizing acids and forming salts, for example :



But the hydroxides are hardly to be called alkalis ; they are only very weak bases. Most of these bases are very insoluble in water, and only one or two of them are strong enough to barely impart to litmus the blue color that is the characteristic effect of bases.

As a class, the heavy metals are far less active chemically than the alkali or the earth-forming metals. They do not react to any great extent with dry air or with pure water, and this freedom from attack is one of the properties that makes them useful metals.

252. Varying Activity of the Heavy Metals.
The heavy metals may be graded according to their chemical activity, and in this respect they fall in the order indicated in the accompanying list.

All the metals standing above hydrogen in this list are more active than hydrogen and can displace that element from acids. Zinc acts vigorously with dilute sulphuric or hydrochloric acid, and hydrogen gas is evolved.

Iron acts somewhat less vigorously. Tin and lead displace hydrogen, only very slowly.

Metals below hydrogen are less active and will not displace hydrogen at all from acids. For example, if a clean piece of copper is placed in dilute sulphuric or hydrochloric acid, no reaction occurs. (It is true that copper reacts freely

Manganese
Zinc
Chromium
Iron
Nickel
Tin
Lead
Hydrogen
Copper
Mercury
Silver
Platinum
Gold

Relative Activ-
ity of Metals

with nitric acid and a gas is given off, — but this gas is not hydrogen.)

The metals higher in the list are not only more active in displacing hydrogen, but they are also more active in combining with non-metals; for example, the oxygen of the air. Bright polished surfaces of iron, zinc, and lead do not remain bright long when exposed to the air, particularly if the air is moist. Copper also tarnishes when exposed to the weather. When the film of oxide first formed on the surface of a metal is impervious, further action of the weather is stopped; whereas if the film is porous, as is the case with iron rust, the corrosion may continue until the metal is all eaten away.

Silver, platinum, and gold, which are known as precious metals on account of their value, are so inactive that they completely withstand the action of the weather.

Both copper and silver coins darken when carried in the pocket, and silver spoons grow black when they are used in eating eggs. This blackening is caused by sulphur compounds which are present in small amounts in the perspiration and in eggs. Copper and silver show a peculiarly strong inclination to form compounds with sulphur, and these sulphides are very black, so that they are very conspicuous on the metallic surface.

Platinum and gold are almost perfectly resistant to corrosion or to attack of any kind. Not only are they unattacked by the ordinary acids, but they are not even acted on by the *oxidizing* acid, nitric acid, which reacts readily with copper, silver, and mercury. As was seen under the topic "*aqua regia*," gold and platinum are, however, attacked by a mixture of hydrochloric and nitric acids. Gold and platinum chlorides are formed by the action, and these com-

pounds being soluble, the metals appear to dissolve in the aqua regia.

253. Occurrence in Nature. According to their activity, we can predict with some certainty which of the heavy metals will be found combined and which uncombined in the earth. The metals above hydrogen are not found uncombined, except that metallic iron is sometimes found in meteorites. These metals are often found in large deposits as oxides, sulphides, and carbonates.

The metals below hydrogen are all found at times uncombined in nature. Copper is more frequently found as the oxide or sulphide. Silver and mercury are found often as sulphide and often in the uncombined state. Gold and platinum are usually found in the uncombined state.

SUMMARY

The metals form a class of elements as distinguished from the non-metals.

The principal physical characteristics by which metals differ from non-metals are that they possess metallic luster and conductivity for heat and electricity.

Chemically, metals are base formers and non-metals are acid formers.

Classes of metals: We have grouped the metals into three main classes; namely, the alkali metals, the earth-forming metals, and the heavy metals.

The alkali metals are extremely active chemically and their hydroxides are very strong bases, the so-called caustic alkalies.

The earth-forming metals are also very active, but they do not furnish such strong bases. Many of their compounds are insoluble in water and earthy in their nature; a large part of the earth's crust is composed of these compounds.

The heavy metals are heavy in weight and inactive chemically in comparison with the other two classes. The heavy metals may be divided into two groups according to their activity:

those standing above hydrogen in this respect and those standing below. The former are found combined, the latter are frequently found free in nature.

Questions

1. How can you tell a metal from a non-metal?
2. Why is hydrogen regarded as a metal in its chemical relations?
3. Can metals unite chemically with metals? What are alloys?
4. Can non-metals unite with non-metals? Give illustrations.
5. What was the basis of the classification of the metals into three groups in this chapter?
6. What are the principal chemical characteristics of the alkali metals?
7. What hypothetical metal is classed with the alkali metals?
8. How do the metals of the earth-forming group differ from those of the alkali group in general physical properties?
9. Into what group would the precious metals naturally fall?
10. Which of the metals would you expect to find uncombined in nature?
11. Which class of metals can best be used for structural work? Why?
12. Which of the heavy metals can best be used for jewelry?
13. Why is zinc, which is a more active metal than iron, superior to iron for use on roofs?
14. Why is the sheet iron used in the canning industry always coated with tin? (Food products often contain weak acids.) Is tin a perfect metal for the purpose?
15. How is the iron of bridges and other structures guarded from corrosion?

CHAPTER XXII

METALLURGY

254. Minerals and Ores. It has been seen in the preceding chapter that the metallic elements, except sometimes copper, mercury, and the precious metals, — silver, platinum, and gold, — are found in nature combined with non-metals. Such compounds, and indeed all pure substances occurring in rocks, are known as *minerals*.

Sometimes large deposits of pure mineral are found, but more often the valuable mineral is found in veins and pockets in other rock, or disseminated through it, and it is impossible to treat the mineral in the metallurgical process without treating also large amounts of worthless rock.

Such a mixture of rock and mineral or native metal is called an *ore* when the cost of mining and extracting the metal from it is less than the value of the metal obtained.

Thus a rock which contains as little as a gram of gold per ton may be considered an ore, if it occurs in a large deposit and in a locality where it can be cheaply handled. Few rocks contain so small an amount of iron as this and many of the common rocks contain several per cent of iron; to be of use as an iron ore the rock must consist almost exclusively of the iron mineral.

In the table on the next page are given the names and chemical formulas of the most important minerals of the commoner metals.

METAL	MINERAL	FORMULA OF MINERAL
Iron	Hematite	Fe_2O_3
	Magnetite	Fe_3O_4
	Siderite	FeCO_3
	Limonite	$\text{Fe}_2\text{O}_3 \cdot 3 \text{H}_2\text{O}$
Copper	Native Copper	Cu
	Chalcopyrite	CuFeS_2
	Cuprite	Cu_2O
	Chalcocite	Cu_2S
Lead	Galena	PbS
Tin	Cassiterite or Tinstone	SnO_2
Zinc	Zinc Blende	ZnS
	Zincite	ZnO
	Calamine	Zn_2SiO_4
Mercury	Cinnabar	HgS
Silver	Native Silver	Ag
	Argentite or Silver Glance	Ag_2S
	Cerargyrite or Horn Silver	AgCl
	Proustite or Ruby Silver	$3 \text{Ag}_2\text{S} \cdot \text{As}_2\text{S}_3$
Gold	Native Gold	Au
	Calaverite	AuTe_2
Platinum	Native Platinum	Pt
Aluminium	Bauxite	$\text{Al}_2\text{O}_3 \cdot 2 \text{H}_2\text{O}$
Nickel	Millerite	NiS
Antimony	Stibnite	Sb_2S_3

IRON

255. Iron is the most important of all the metals. Its cheap production and the development of different grades such as cast iron, wrought iron, and steel, varying in hard-

ness and strength, have made possible the enormous growth of railroads, the development of building construction, and the expansion of industrial operations within recent years.

Although iron is found abundantly in nature as sulphide and silicate and to some extent as carbonate, only a very small amount of the

iron produced comes from these sources.

The principal ores are the oxides, which frequently occur in extensive deposits and can be mined cheaply on a large scale. The

metallurgical treatment of the oxide ores is also comparatively simple, for the oxygen is readily re-

moved when the ore is heated with some form of carbon. Charcoal is used in a few places for this purpose, but coke is more commonly used. To make iron as cheaply as is to-day demanded, operations must be carried out on a large scale so that all possible economies may be introduced.

256. Blast Furnace. The reduction of the iron ore is carried out in a blast furnace (Figure 42). Blast furnaces are often built as high as 100 feet; they consist of a steel shell lined with fire brick. Since the ore, the coke, and other materials which must sometimes be mixed with the ore are put into the furnace from the top, it is necessary to provide some form of hoisting apparatus.

The rock which is associated with the iron oxide in the ore



FIG. 41. — Hematite.

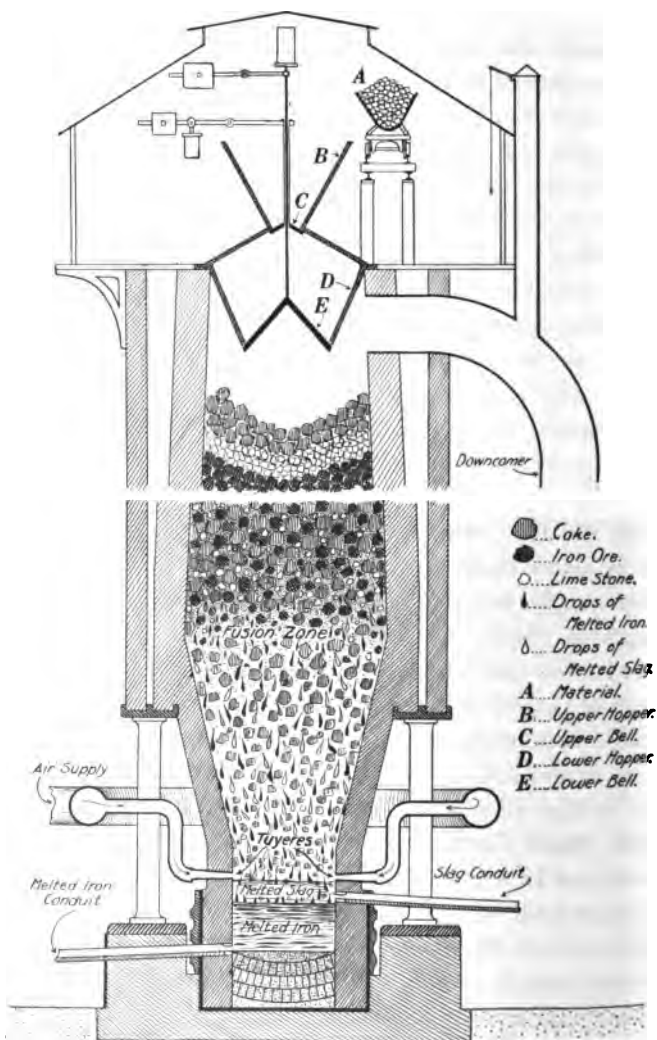
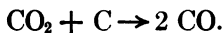


FIG. 42. — Blast Furnace.

does not melt easily, and it is necessary to add something which will unite with it and form more fusible compounds. (Notice that the blast furnace has no grate at the bottom for shaking out the ashes, — only two holes through which liquids may be withdrawn.) Anything which will thus form a fusible mixture with the worthless rock is called a flux. The rock is usually composed mostly of silicon dioxide with considerable aluminium oxide, and other oxides are united with part of the silicon dioxide in the form of silicates. Aluminium silicate forms the principal part of ordinary clay. The silicon dioxide which is not combined with the other oxides is nothing but common quartz. This is an acidic oxide and, as we would suppose from our study of acids and bases, a proper flux for it is a basic oxide. Limestone is always used for this purpose in the iron blast furnace. The calcium carbonate, of which it is composed, is changed by the heat into calcium oxide (lime), which unites with the quartz and other oxides in the charge and forms a fusible silicate. When the latter flows from the furnace and cools slowly in the air, it looks much like pumice stone; when it cools rapidly, it looks like glass. Indeed it is not unlike glass in character. It is known as the slag.

The coke serves a double purpose, first to reduce the iron oxide, and second to act as a fuel and melt both the reduced iron and the slag. A small part of the carbon of the coke is dissolved in the molten iron. Heated air is blown under a high pressure through the pipes, known as the tuyeres, entering near the base of the furnace. The coke meeting this air blast is burned to carbon dioxide, but this gas passes up through the heated coke and is reduced to carbon monoxide,



The carbon monoxide passing through the hot iron oxide in the middle part of the furnace reduces it,



This reaction, however, is a reversible one, as indicated by the double arrow, and it only proceeds in the desired direction towards the right so long as an abundance of carbon monoxide compared with the amount of carbon dioxide is present. Consequently, the escaping gases have a large content of carbon monoxide; the amount usually exceeds 20 per cent by volume of the total gas and it possesses about one half the heating value of the coke used in the furnace. The blast furnace gas is burned outside of the furnace to heat boilers, and to preheat the air blown into the furnace. It is also used in gas explosion engines to furnish power.

The ore and limestone are mixed and fed with alternate layers of coke into the top of the furnace. The charge gradually sinks through the shaft and undergoes various changes as it approaches the point where the air enters, which is the hottest part of the furnace. In the upper part it is merely heated and dried; in the central part most of the reduction takes place, but the heat is not intense enough to melt the iron. As the charge descends into the narrower part of the furnace it becomes very hot and the iron alloys with some of the carbon. Now pure iron melts only at 1520°C. , a temperature which is hardly reached in any part of the furnace; but iron alloyed with a few per cent of carbon melts as low as 1125°C. The molten iron sinks into the crucible at the bottom of the furnace. The flux and foreign rock melt together as slag, which floats on the molten iron and protects it from the oxidizing influence of the blast.

At the bottom of the crucible is the metal tap through

which the molten iron is withdrawn about every six hours. At other times the tap is kept closed. Above this is the slag tap through which the molten slag is withdrawn every two hours. The iron may be either cast into molds, forming what is called pig iron, or it may be converted into steel as described below. The slag is sometimes thrown away and sometimes used for making cement.

257. Cast Iron. The direct product of the blast furnace is not pure iron. It contains 3 to 4 per cent of carbon, sometimes as much as 3 per cent of silicon — from a reduction of some of the silicon dioxide — and manganese, phosphorus, and sulphur, if the ore contained these elements. This impure iron melts easily and is useful in making castings, but it is brittle and lacks strength.

Nevertheless it is able to resist crushing and it is largely used in making supporting columns to sustain great weights in buildings. It is also used for engine bases and supporting structures for heavy machinery. Since it expands at the moment of solidifying, it is forced into every corner of the mold and very sharply defined castings are thus obtained. On account of its cheapness and the facility with which it is made into castings enormous quantities are used where brittleness is not too objectionable a feature.

MANUFACTURE OF STEEL

The carbon in excess of 2 per cent together with the silicon and some of the other impurities in pig iron make it brittle and weak and unsuitable for many purposes. These impurities, which are due to the reducing action in the blast furnace, can be removed by an oxidizing process.

258. Bessemer Process. This method, which takes its name from the inventor, is carried out in the so-called Besse-

mer converter, Figure 43. The converter, which may hold as much as 20 tons of metal, is a steel shell lined with silicious material; but when the metal contains much phosphorus or sulphur it is necessary to make the lining of burnt dolomite (limestone containing magnesium carbonate in addition to calcium carbonate). When the silicious lining is used, the

method is called the acid process; and when the dolomite lining is used, the method is called the basic process.

The converter is partly filled with molten iron from the blast furnace, and air under high pressure is forced into the hollow place in the bottom, from which it passes through small perforations into the molten metal. The

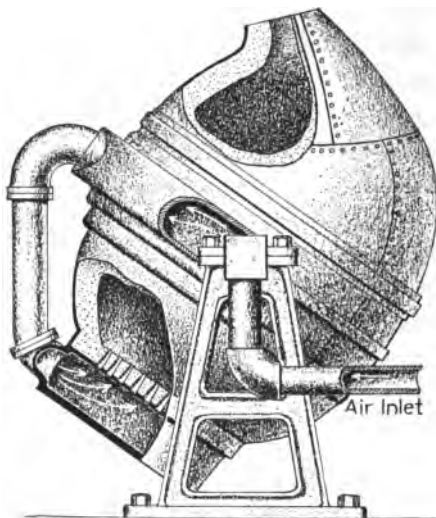


FIG. 43. — Bessemer Converter.

impurities are more easily oxidized by the air than is the iron. The silicon and manganese oxides formed (and magnesium phosphate in the basic process) float as molten slag on the surface of the metal, and the carbon passes off as monoxide gas. The heat produced in burning these impurities is sufficient to keep the charge in a fluid condition. The disappearance of the carbon flame indicates that the oxidation is completed. It is impossible to stop the process when the carbon is reduced to just the desired per cent, so it is

customary to burn off all the carbon and then add the necessary amount in the form of an alloy of iron, manganese, and carbon. The manganese improves the quality of the product.

After the iron has been recarburized, the converter is tipped, and the contents, which are now in the form of steel, are poured into large ladles from which the ingot molds are filled.

259. Open Hearth Process. This is carried on in a furnace such as is shown in Figure 44. Some of these furnaces will hold 75 tons or more of charge. The hearths are lined

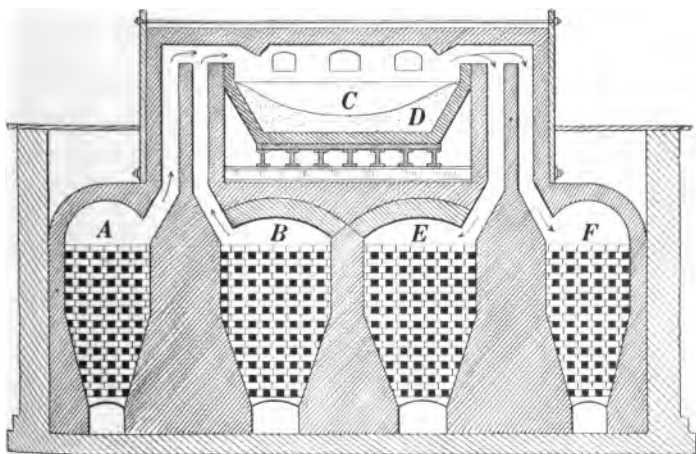


FIG. 44. — **Open Hearth Furnace.** Gas (A) and air (B) after passing over hot bricks enter the furnace together. The iron (C) rests upon the hearth lining (D). The hot gaseous products heat the bricks in E and F which are later made the inlets in order to preheat the entering gas and air.

with the same materials used for converter linings. They are heated by burning gas above the charge; both the gas and the air which is necessary to burn it are previously heated by passing over hot bricks below the furnace, thus increasing the furnace temperature.

The material used for making steel in these furnaces is a mixture of pig iron, scrap iron or steel, and oxide iron ore.



FIG. 45. — Open Hearth Furnaces. Pouring Ingots.

The scrap dilutes the impurities in the pig iron, but most of the impurities are removed by oxidation, due partly to the oxygen in the air and partly to the oxygen of the iron oxide. When a sample shows that the impurities are suffi-

ciently removed, the charge is withdrawn into ladles, carburized if necessary in the same manner as in the Bessemer process, and then cast into ingots. Since it is impossible to take samples during the treatment in the Bessemer converter, the process cannot be so well regulated as the open hearth process, where frequent samples may be taken and a definite product obtained. For this reason, open hearth steel is usually considered more reliable than Bessemer steel.

260. Uses of Mild Steel. Steel containing less than 0.3 per cent of carbon is known as mild steel. Most of the steel produced by the Bessemer and open hearth processes is of this kind, and it is used in tremendous quantities for railroad rails, for structural work in buildings and bridges, for wire fences, for telegraph wires, and for rolling into sheet metal. The sheet metal may be used uncoated for many purposes. For so called tin cans it is coated with tin to protect it from oxidation and from the action of the food products which may be put up in the cans. Sheet iron or steel is coated with zinc (galvanized), especially when it must resist the corrosive action of a damp atmosphere. Sheet iron for house furnaces in damp cellars and for roofing purposes is always galvanized.

Great strength and toughness combined with a considerable degree of hardness characterize mild steel and give it its great usefulness.

261. Special Steels. Steels may contain amounts of carbon between 0 and 1.5 per cent. In general, the higher the carbon, the harder the steel, but the heat treatment (tempering, annealing, etc.) has a great effect in determining the hardness.

High carbon steel for tools, watch springs, razor blades, and the like requires special treatment and is made on a

much smaller scale and by a more expensive process than common steel.

Of the other elements than carbon added to give special properties may be mentioned chromium, which gives a very hard steel used in making burglar-proof safes, and nickel, which gives a tough steel used for the armor plate of warships.

WROUGHT IRON

262. The process by which most of the wrought iron is made is called the puddling process. The furnace used resembles slightly the open hearth steel furnace, but it has a fire box at one end where coal, oil, or gas is burned and the flame passes over the charge to the flue at the other end.

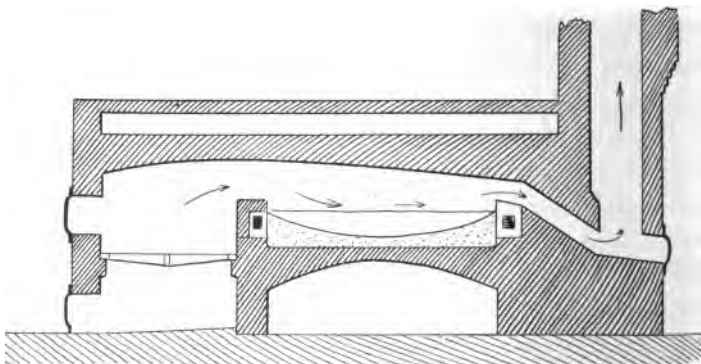


FIG. 46. — Reverberatory Furnace.

This type of furnace is called a reverberatory furnace because the roof is so constructed as to deflect or reverberate the heat of the flame down on the charge. Modifications of it are used in various other metallurgical processes.

The hearth of the puddling furnace is lined with blocks of oxide iron ore. The pig iron is usually charged in the solid

form and melted in the furnace. The oxygen of the lining and of the atmosphere unites with the impurities in the charge, the carbon passes off as carbon monoxide, and the other oxides combine to form slag. The iron, which is now nearly pure, has a much higher melting point than the original pig iron and instead of being liquid is in a pasty condition. The men in charge of the furnace, with tools made for the purpose, now stir the charge, mixing slag and iron together and then divide it into several balls which can be removed from the furnace with tongs suspended from a traveling pulley. These balls are passed through machines which squeeze out most of the slag and finally roll the iron out into the rods and bars of commerce.

263. Uses of Wrought Iron and Very Low Carbon Steel.

Pure iron, unlike the impure material, corrodes but slowly. It is rather soft, being easily scratched with a knife, highly ductile and malleable, but still it has a fair degree of tenacity. It is very useful where great toughness combined with considerable strength is required.

Wrought iron is almost pure iron. It softens sufficiently for welding below 1000 C. although it does not melt below 1500° C. In this it is very different from cast iron, which does not soften before it melts. Wrought iron is therefore suitable for forging — it is the metal used by the blacksmith — and the slight admixture of slag that it contains gives it a fibrous structure which seems to increase rather than detract from its usefulness for forging. Wrought iron probably resists corrosion better than any other form of iron and this property seems to be due to its freedom from carbon.

Wrought iron, however, is more costly than mild steel and in recent years a steel unusually low in carbon, sometimes called "ingot iron," has been prepared in large amounts and is

coming into use for wire fences and many other objects which must have a high resistance to corrosion when exposed to the weather. It is a fact of common knowledge that some wire fences resist corrosion for years, whereas others are badly corroded in a few months. The difference can almost always be traced to the quality of the iron.

COPPER

264. Native copper is found abundantly in the Lake Superior mines in northern Michigan. It is also found in some



FIG. 47. — Native Copper.

other places, but not in workable quantities. The rock in which the native copper is imbedded is crushed, and the copper particles are separated from the rock by a washing process

which is based on the higher specific gravity of the copper. The metal is then melted and cast into ingots.

Copper is found in nature principally as the sulphide, and it is usually associated with iron sulphide and other sulphides. The upper layers of great copper deposits are often found to consist of the oxide and the carbonate, but as the mines are deepened the ore always changes to sulphide. The oxygen and carbon dioxide in the air, assisted by percolating waters, acting for thousands of years, have worked down to some depth and slowly oxidized the original sulphide.

Copper is obtained from the sulphide ores in two steps. The first step is to eliminate all of the waste rock and part of the iron and sulphur, thus producing copper matte, a

mixture of the sulphides of copper and iron. This may contain varying amounts of copper up to 80 per cent, but usually between 20 and 40 per cent. The next step is to oxidize all the remaining iron and sulphur, leaving metallic copper.



FIG. 48. — Chalcopyrite.

The first step may be performed either in a reverberatory furnace or in a blast furnace. The latter resembles the iron blast furnace, but is much smaller. The second step is to treat the molten matte in a converter similar to the Bessemer steel converter, except that instead of being admitted at the bottom the air is blown in at one side a short distance above the bottom. The oxygen of the air unites with the sulphur and the iron; the sulphur dioxide passes off and the iron oxide unites with the silicious lining of the converter, or with silicious material thrown into the matte, and forms slag. When the impurities are oxidized as far as possible, the slag is poured off and the copper cast into cakes for refining.

Oxide ores may be reduced directly to metallic copper in the blast furnace.

265. Refining of Copper. The copper obtained from the furnaces invariably contains other metals, including gold and silver. The most important use of copper is as a conductor of electricity. Even small amounts of such good conductors as gold and silver alloyed with copper impair its conductivity;

and other elements, notably arsenic, impair the conductivity to a still greater degree.

Crude copper may be refined either in a reverberatory furnace or by an electrolytic method. The former is an oxidizing process which slags most of the impurities and is used when the arsenic and precious metals are low; the latter are not as easily oxidized as the copper itself. The electrolytic method removes practically all of the impurities; and since the gold and silver can be saved, it is always used when there is a sufficient quantity of these metals present to warrant the extra expense of the process. The main operations are as follows:

The copper is cast in plates about two inches thick and four feet square which are hung alternately as positive elec-

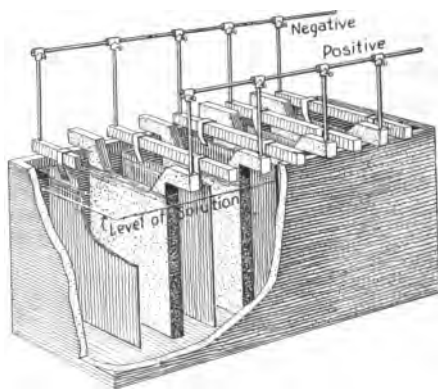


FIG. 49. — Electrolytic Refining of Copper.

trodes in a bath containing copper sulphate and sulphuric acid. Alternating in the bath with these plates are thin plates of pure copper, all connected with the negative conductor of the electric circuit. In Figure 49 we have shown five negative and four positive

plates. In one of the large refining works, they put twenty-three negative and twenty-two positive plates in one tank. One building has sixteen hundred of these tanks in operation. The current in passing dissolves copper from the positive electrode, takes it through the solution, and deposits

it upon the negative plates. The impurities either do not dissolve at all or else they pass into solution and remain in the solution. The insoluble impurities, among which are all the gold and silver, simply drop to the bottom of the tank as the electrode is eaten away. The mud from the bottom is worked up for gold and silver and yields a valuable profit.

266. Uses of Copper. Copper is ductile, tough, and resistant to corrosion, and it has the highest electrical conductivity of any metal except silver. It is used to a very large extent in electrical work, — for telephone, electric light, and trolley wires, and for the coils of all electrical machines.

Its resistance to corrosion makes it a useful metal for exposed corners and edges of roofs, for water conductors, and cooking utensils.

Copper is an important component of many useful alloys, notably brass and bronze. Brass usually contains about two thirds copper and one third zinc.

LEAD

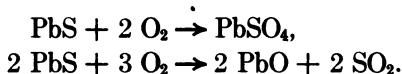
267. By far the commonest ore of lead is galena, or lead sulphide. It is a beautifully lustrous gray crystalline substance, and it is often found crystallized in almost perfect cubes.

The metallurgical treatment of lead sulphide is similar in principle to that of copper sulphide. One method is to roast it

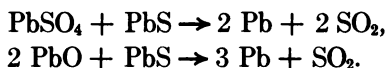


FIG. 50. — Galena.

in a reverberatory furnace so as to burn the sulphur and leave uncombined lead. The process is not carried out, however, in a single operation. It is usually roasted first with free access of air whereby only a part of the ore is oxidized. Part of the lead sulphide so attacked is changed to lead sulphate and the other part to lead oxide and sulphur dioxide.



The air is then cut off and the temperature is raised, whereby the unchanged lead sulphide reacts with the lead sulphate and lead oxide, yielding metallic lead and sulphur dioxide.



Another method is to treat the ore with coke and fluxes in a blast furnace. The products of this furnace are slag, lead matte, and metallic lead.

The crude lead obtained by either of the above methods may carry considerable amounts of silver and gold, in which case it is refined by special processes designed to save these metals. The amount of silver obtained in this way is of great importance.

268. Uses of Lead. Lead, owing to its high degree of resistance to the action of water and of some acids, is used for water pipes, coverings of wire cables in conduits, tanks and containers for various liquids, and for the chambers in which sulphuric acid is made.

Lead salts are extremely poisonous, and the use of lead for conveying drinking water is open to objection. Although no harmful amount is dissolved by hard water, nevertheless

soft water, particularly rain water, dissolves sufficient lead oxide from the pipes to cause serious danger.

Lead melts very easily; alloyed with tin it makes solder.

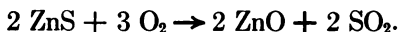
With antimony lead forms the alloy called type metal.

The great density of lead early led to its use in bullets and shot.

Large amounts are also made into white lead, a basic carbonate of approximately the composition $\text{Pb}(\text{OH})_2 \cdot 2 \text{PbCO}_3$, which is used in paints.

ZINC

269. The most important ore of zinc is zinc sulphide. This is roasted, whereby it is changed to oxide.



The sulphur dioxide given off is commonly utilized to make sulphuric acid, as indeed is also sometimes done at lead and copper smelters. The zinc oxide is mixed with crushed coal and heated in retorts.



Zinc is a volatile metal when compared with copper, lead, and iron. Zinc vapor consequently passes from the retort together with the carbon monoxide. It is condensed to liquid zinc, which is run into molds to solidify.

Some ores which are not suitable for the production of metallic zinc are heated on a grate with coal, and the gases after cooling are filtered through cloth. The zinc is thus recovered as zinc oxide, a white powder, which has a ready sale to paint and rubber manufacturers.

270. Uses of Zinc. Zinc is one of the most active of the heavy metals, as is evidenced by the vigor with which it

displaces hydrogen from acids. Hence arises its use in battery cells such as are used for ringing electric bells. It is the zinc rod or plate in such cells which is eaten away.

In view of the great chemical activity of zinc it may seem strange that it is so little attacked by the weather, and that it is used to galvanize iron and thus to protect the less active metal. The secret of its resistance to corrosion is that it quickly becomes coated with a thin impervious layer of oxide, which excludes air and dampness from the metal beneath.

MERCURY

271. The sulphide ore of mercury is roasted in furnaces with access of air. The sulphur burns to sulphur dioxide, and the mercury, which is but an inactive metal, is left uncombined. It distills with the heat, and mercury vapor passes with the gases into a condensing chamber from which the liquid mercury is obtained.

SILVER

272. A large part of the world's supply of silver, as already noted, is obtained as a by-product from the production of lead and copper.

Apart from some native silver, the important ores which are worked for silver alone are the sulphide, arseno-sulphide, and the chloride. Many different processes are employed for treating silver ores; the one to be described is perhaps typical.

The crushed rock containing sulphide ore is mixed with common salt and roasted, whereby the silver sulphide is changed to chloride. Silver chloride is insoluble in water but is soluble in a dilute solution of sodium thiosulphate.

The roasted sulphide ore, or the chloride ore direct, is treated with sodium thiosulphate solution and the liquid is then run into tanks and the silver precipitated as sulphide by adding sodium sulphide. The insoluble silver sulphide is recovered by filtering, and silver is obtained from this by burning off the sulphur.

The cyanide process as described under gold is also extensively used for silver ores.

GOLD

273. Gold is usually found in the uncombined condition, but in exceedingly small particles disseminated throughout masses of rock. Most of the gold can be recovered by finely crushing the ore in stamping machines and washing it with water through a shallow trough, the wide flat bottom of which consists of a copper plate coated with mercury. When the gold comes in contact with the mercury, it amalgamates with it, while the waste material passes on. The plates are scraped periodically and the gold is recovered from the amalgam by distilling off the mercury.



FIG. 51. — Native Gold.

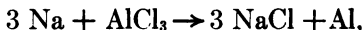
Some ores can be more successfully treated by a chemical method. The one most used is the cyanide process, in which the finely crushed ore is treated with a solution of potassium cyanide which, together with oxygen of the air, reacts with the gold, producing a soluble compound. The solution is run

into tanks filled with zinc shavings. It has already been noted that zinc is a more active metal than gold. Here again this fact is shown, for the zinc passes into the solution, forcing the gold to precipitate as free metal. This finely divided gold is then melted and cast into bars.

ALUMINIUM

274. Aluminium oxide cannot be reduced to metallic aluminium by means of carbon in a blast furnace because of the very great chemical activity of the element. Aluminium oxide will react with carbon at a very high temperature, but aluminium carbide and not the uncombined metal is obtained.

Formerly aluminium was obtained by treating aluminium chloride with sodium,



but this method is now entirely superseded by the electrolytic method.

Aluminium oxide can be melted only at a very high temperature, but cryolite, a mineral of the formula

$3 \text{ NaF} \cdot \text{AlF}_3$, melts very easily, and, furthermore, will dissolve aluminium oxide much as water will dissolve common salt. In the electrolytic process cry-

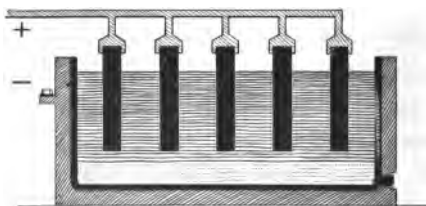


FIG. 52. — Electrolytic Production of Aluminium.

olite is melted in iron vats lined with carbon, aluminium oxide is added, and carbon electrodes are introduced. The current enters through the carbon electrodes and passes out

through the iron vats. The resistance to the passage of the current causes heating sufficient to keep the charge melted. Oxygen is liberated at the carbon electrode and either escapes or burns the carbon to carbon monoxide. The aluminium is liberated at the surface of the carbon lining and sinks in the melted condition to the bottom of the bath, where it is occasionally tapped off. The process is continuous and fresh aluminium oxide is added as fast as that in the bath is decomposed. The cryolite suffers no change.

The chief ore of aluminium is bauxite, a rather impure aluminium oxide containing water. For the best grade of metal, this ore must be purified chemically so that only pure aluminium oxide shall be introduced into the electrolytic bath.

275. Uses of Aluminium. Aluminium is the lightest of the metals which are strong enough and resistant enough to corrosion to be useful for objects to stand wear and weather. The resistance to corrosion does not arise, however, from its chemical inactivity, but rather from the fact that it coats itself with a very impervious film of oxide. The truth of this statement is shown by an interesting experiment. If a piece of aluminium is carefully cleaned with hydrochloric acid and a little mercury is rubbed on the surface, it amalgamates. Soon a white fluffy powder, aluminium oxide, is seen to form over the amalgamated surface and to increase quite rapidly in bulk. Before long the aluminium has entirely disappeared, a little globule of mercury is left, and a heap of the fluffy powder. On the surface of the amalgam the aluminium oxidizes as well as on the surface of the pure metal, but the oxide does not adhere to the liquid surface; it floats off and therefore the oxidation continues.

Aluminium is not as cheap as steel, and its use is confined mostly to articles in which lightness is a prime essential, such as parts of automobiles and flying machines. Aluminium serves excellently for cooking utensils. It is a very good conductor of heat and electricity and it is sometimes used in place of copper for electric conductors.

SUMMARY

Metals in Nature: All metals except the chemically inactive ones, such as copper, silver, gold, and platinum, are found in nature always in combination with non-metals, most often with oxygen and sulphur. Gold and platinum are almost always, and silver and copper are sometimes, found uncombined.

Metals from Ores: Oxygen can be removed from combination with most of the heavy metals by means of carbon, for the heavy metals are, in the main, not very active chemically.

The sulphides can be converted into oxides by roasting, whereby sulphur dioxide escapes.

Oxides of the very active metals like aluminium, sodium, potassium, magnesium, and calcium cannot be reduced with carbon and obtained as uncombined metals. Recourse is usually had in these cases to electrolysis of their fusible compounds.

Questions

1. Suggest a method to obtain metallic tin from tinstone.
2. What metals can be obtained from their oxide ores by reduction with carbon? What ones cannot?
3. What method is available for separating the metal when the oxide cannot be reduced with carbon?
4. How might mercury be obtained from mercuric oxide without using carbon?
5. Explain how aluminium oxide is brought into the liquid condition previous to the separation of the metal by electrolysis.
6. How are gold and silver extracted from the crude copper from the smelter?

7. When refuse rock from copper mines is heaped up and kept moist, any copper sulphide present oxidizes slowly to copper sulphate, which is soluble. How might metallic copper be obtained from the solution draining from the bottom of the heap?

8. Calculate the per cent of iron in each of the four minerals, Fe_2O_3 , Fe_3O_4 , FeCO_3 , and $\text{Fe}_2\text{O}_3 \cdot 3 \text{H}_2\text{O}$.

9. What weight of carbon would be necessary to reduce (a) 1000 kilograms of cuprous oxide, Cu_2O , (b) 1000 kilograms of cupric oxide, CuO , assuming the carbon is all changed to carbon dioxide in the process and neglecting the amount of fuel which must be burned to supply heat.

10. What weight of carbon is needed to reduce 1000 kilograms of zinc oxide? The carbon is oxidized only to carbon monoxide.

CHAPTER XXIII

COMPOUNDS OF CARBON

WE have already become familiar with some of the properties and some of the compounds of carbon. We have seen that carbon enters into a continuous cycle of changes between living and inorganic matter. Fuels, — wood, coal, charcoal, — which are without exception the product of present or past organic life burn, and the carbon in them yields the gas carbon dioxide. Plants take carbon dioxide from the air through the surfaces of their green leaves and with the aid of the energy obtained from sunlight convert it into the most complex and varied compounds containing sometimes oxygen and hydrogen and sometimes nitrogen in addition. These compounds in time always yield carbon dioxide back again to the air, for they are either burned directly as fuel, or they are eaten by animals and burned slowly in the animal tissues, or they decay, which is also a process of slow combustion.

In the present chapter we shall deal mainly with carbon as it exists in substances which are not closely related to living things. In Chapter XXIV, a brief view will be given of a few of the more important of the compounds of carbon, which are formed like starch and sugar directly in life processes, or are at least derived from compounds so formed.

UNCOMBINED CARBON

There are three different forms in which uncombined carbon exists, namely, amorphous carbon, which, as the name implies, is without definite form or shape, and two different crystalline forms, graphite and diamond.

276. Amorphous carbon is without crystalline structure and in that sense it is without form. Masses of it may, of course, exist in any shape, but there is no evidence within the mass of any tendency to a definite structure. Amorphous carbon is obtained when organic matter is decomposed by great heat. The carbon is left as a charred mass, while the other elements of the compound are driven off as volatile matter. Charcoal, coke, lampblack, and gas carbon are well-known varieties of amorphous carbon.

Charcoal is obtained by heating wood in the absence of air; a number of volatile products, including water, wood alcohol, acetic acid, acetone, and tar, are driven off, and with these products escape all of the hydrogen and oxygen as well as a portion of the carbon of the wood, while charcoal is left as a non-volatile residue. Charcoal is nearly pure carbon, except that it still contains the mineral matter of the wood. All ordinary kinds of charcoal, therefore, leave a little mineral ash when they are burned.

Coke is obtained from soft coal in much the same manner as charcoal is obtained from wood. The volatile products driven off are mainly illuminating gas, coal tar, and ammonia.

Lampblack is familiar to all who have seen a smoking kerosene lamp. It is manufactured by allowing petroleum oil or natural gas to burn with an insufficient supply of air. The heat of the flame decomposes the compound; the hydrogen burns and maintains the flame, while a large part of the

carbon remains in extremely small particles as soot or lampblack. This adheres to a cooled surface which continually revolves just above the flame. A scraper bears upon another part of the revolving surface and scrapes off the lampblack into an appropriate receptacle. Lampblack is much used as a pigment in paints and especially in printer's ink.

Gas carbon is formed in the retorts in which soft coal is destructively distilled in the manufacture of illuminating gas. It is formed where the gas comes in contact with the white-hot top and sides of the retort and is there decomposed. Being formed at a higher temperature, it is harder and more compact than lampblack. It is largely used in the manufacture of electric-light carbons.

277. Coal. Coal is not pure carbon, but it consists very largely of carbon. It is a product of the decomposition of trees and plants which grew in a long-past geologic age. By floods or other natural agencies, the luxuriant vegetation of the so-called carboniferous period of the earth's history became covered with deep layers of earth in some localities before it had a chance to fully decay. Deep down beneath the earth's surface, heat and pressure have in the course of centuries changed the original organic material into coal. Coal still contains some of the hydrogen, oxygen, and nitrogen of the original organic matter; soft or bituminous coal contains a considerable amount; hard or anthracite coal contains much less.

278. Graphite. We have seen above that the residue obtained by artificially heating coal in coking ovens is coke, one of the varieties of amorphous carbon. The final product of a similar process in nature is graphite. Where coal has been very deeply buried and consequently subjected to more of the earth's interior heat, as well as enormous pressure, the

decomposition has been more complete. The result of this decomposition when carried to its final stage is graphite.

Graphite is found in nature crystallized in soft hexagonal plates or prisms. Its specific gravity is 2.25; it is considerably more dense than amorphous carbon. It is exceedingly soft and offers but little friction when rubbed; on account of this property, it is much used as a lubricant. It is black and opaque and it conducts electricity. It is much used in electrical work on account of its conductance and its low coefficient of friction.

The most familiar use of graphite is in "lead" pencils, for which purpose it is mixed with clay to give the desired degree of hardness and then molded into the "leads."

Graphite is very resistant to heat, so that it is an excellent material for making crucibles, electrodes, and linings in furnaces in which high temperatures are employed. It is extremely hard to make graphite burn. The harder an anthracite coal, the more difficulty there is in getting it to burn, and when the coal is graphitic in nature, it scarcely burns at all in a furnace.

In pure oxygen, a complete combustion of graphite can be effected, and the only product of the combustion is carbon dioxide. It is thus made certain that graphite is composed only of carbon.

Graphite is now made artificially in an electric-furnace process in which an enormous current is sent through a furnace packed with anthracite coal. The current produces the temperature of the electric arc; the coal is completely decomposed and all the ordinarily volatile matter and even the mineral matter, which in an ordinary furnace is involatile, are expelled as vapor. Carbon alone is left as a residue, and this is changed into the form of graphite.

279. Diamond is the most beautiful and the rarest as well as, perhaps, the most interesting form of carbon. It is just as much pure carbon as are graphite and amorphous carbon, as can be proved by burning it in oxygen; it gives only carbon dioxide, and a given weight of diamond gives exactly the same amount of carbon dioxide as the same weight of either of the other forms of carbon.

One would never suspect from their physical properties that diamond and graphite are both composed entirely of



FIG. 53. — **Diamond.**
(Natural Crystal.)

the same element, for no two substances could be more dissimilar. Diamond is the hardest substance known, whereas graphite is one of the softest of solid substances. Diamond is colorless, transparent, and a non-conductor of electricity, whereas graphite is black, opaque, and a conductor of electricity. The diamond is insoluble in all known liquids under ordinary conditions of temperature and pressure. Diamond crystallizes in the regular system, usually in octahedra, whereas graphite crystallizes in hexagonal plates.

Diamond has a specific gravity of 3.51, and it is thus by far the densest form of carbon. When it is intensely heated in the absence of air, it swells and becomes black graphite, but when heated intensely in oxygen, the diamond burns completely, producing only a gaseous product.

The differences between diamond, graphite, and amorphous carbon are believed to be due to the same causes as the difference between ozone and ordinary oxygen, that is, to a difference in the number of atoms in the molecule and possibly, also, to the way in which the atoms are linked together.

It was discovered by Moissan, the French chemist, that diamonds of microscopic size can be made artificially by allowing carbon to crystallize from solution in a molten material kept under great pressure. Carbon dissolves to a considerable extent in molten iron. If a mass of molten iron saturated with carbon is suddenly chilled, the outer layers solidify, while the inner portion remains liquid. The latter afterwards solidifies more slowly, and since iron containing much carbon expands on solidifying, it exerts a great pressure against the already solid exterior of the mass. The dissolved carbon crystallizing out under this great pressure assumes the form of diamond. Under ordinary pressure, the carbon separates as graphite. By dissolving away the iron with acid, one can obtain the tiny diamond crystals, but all that have ever been made in this way are too small to be of value.

There is geological evidence that the natural diamonds of South Africa have crystallized from solution in molten rock subjected to enormous pressure.

280. Uses of Diamonds. Aside from its beauty when cut as a gem, diamond is of use in the industrial arts on account of its great hardness. The poorer stones that cannot be made

into gems are set in solder on the edges of great saws that are used for stone cutting; similarly, they are set at the bottom of tubular drills that are used for making deep borings in rock. Diamonds are used

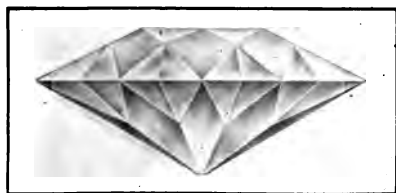


FIG. 54. — **Diamond.** (Cut Gem.)

in the jeweled bearings of delicate instruments of precision. Wires of exact dimensions are made by drawing the metal through perforations in thin plates of diamond.

CARBON AND OXYGEN

We have already seen in Chapter IV that carbon burns in a plentiful supply of oxygen to form carbon dioxide, but with a restricted supply it forms carbon monoxide.

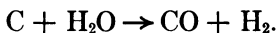
281. Carbon dioxide is the anhydride of carbonic acid, H_2CO_3 , a comparatively weak acid, but still one that is capable of forming salts with all strong bases. A vast amount of carbon dioxide is thus held in the mineral world in combination with various bases. Calcium carbonate is the most plentiful of the carbonates. Limestone, marble, and shells of marine animals are natural forms of this substance. Magnesium carbonate is also very abundant; carbonates of iron, lead, and copper are abundant and constitute valuable ores of these metals.

282. Carbon monoxide is not acidic in nature, as is the dioxide; it therefore does not combine with bases, and we never find it fixed as a component of any of the solid matter of the earth's crust. Its most striking properties are its poisonous character and its combustibility.

The escape of carbon monoxide into living rooms, either from charcoal fires, from faulty furnaces, or from illuminating gas cocks, is a source of grave danger.

Carbon monoxide is so combustible and yields so much heat in burning that in spite of its poisonous character great quantities of it are made and used admixed with other gases as fuel. Pure carbon monoxide burns with a pale blue flame and yields carbon dioxide.

283. Water gas is essentially a mixture of equal volumes of carbon monoxide and hydrogen. It is made by blowing steam through incandescent carbon with which it reacts according to the equation:



In the process of making water gas for lighting in large cities, coke or anthracite coal is placed in large vertical cylindrical furnaces (generators) and kindled at the bottom. Air is blown in until the fire has heated the whole mass to incandescence. Then the air is cut off and steam is blown in and

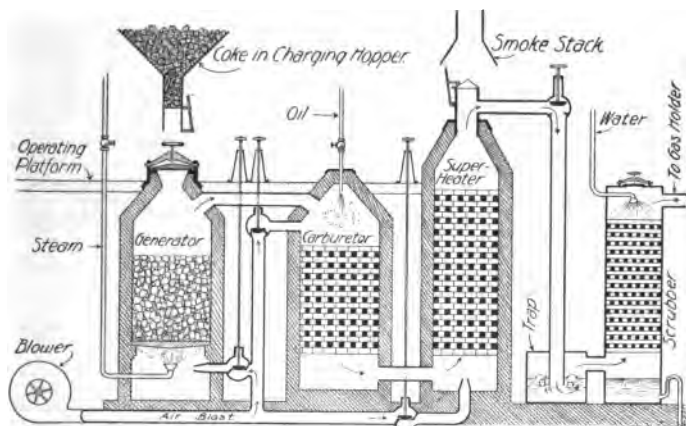


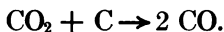
FIG. 55. — Manufacture of Water Gas.

the water gas is produced. When the furnace has become partly cooled by this last process, the gas formation ceases, and the mass must be again heated by blowing in air.

Since hydrogen and carbon monoxide both burn with nearly colorless flames, water gas cannot be used by itself for illuminating purposes. Illuminants are usually added to it by "cracking" petroleum oil. The gas is led through a chamber (the carburetor) containing a checkerwork of white-hot fire brick over which petroleum oil drops. The heat decomposes the oil vapor as it passes through the superheater and permanent gases of high illuminating power are thereby formed.

284. Producer Gas. When air enters from the bottom of a deep anthracite coal or coke fire, carbon dioxide is, without

doubt, formed in the lower layer. As this gas rises, however, it passes through other layers of white-hot carbon and is thereby reduced to carbon monoxide.



The long, pale blue flames seen rising from an anthracite fire, in an ordinary house furnace, are due to the burning carbon monoxide.

The heat developed, when carbon monoxide burns to carbon dioxide, is more than twice as great as that set free when carbon burns to carbon monoxide. It is obvious, then, that to obtain anything like the full heating value of the coal,

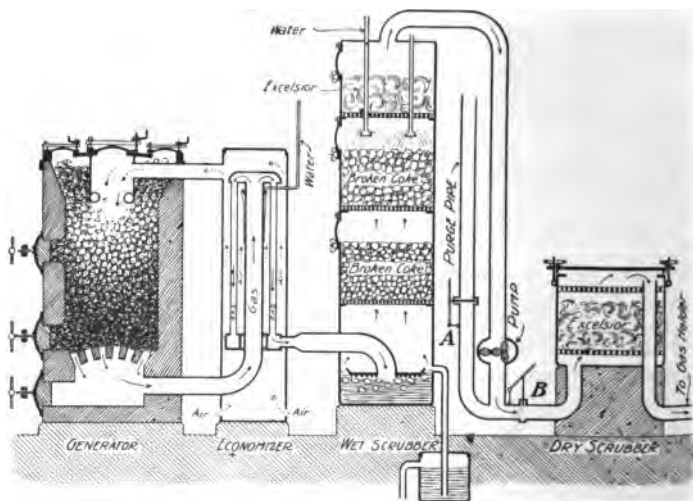


FIG. 56. — Manufacture of Producer Gas.

enough air must be admitted through the upper door of the furnace to completely burn the carbon monoxide.

Gas that is formed in a manner similar to this is used extensively in metallurgy and other industries, and is known

as producer gas. Air is drawn through a very deep coal fire in the generator. The resulting gas mixture contains all the nitrogen of the air, but all of the oxygen has combined with carbon to form carbon monoxide. The gas is conducted through pipes to the furnaces where it is to be burned as fuel. By the process as so far outlined, it is apparent that the heat developed by the addition of the first unit of oxygen to the carbon would be wasted. By moistening the in-going air as it passes through the economizer or by introducing a carefully regulated quantity of steam into the furnace, together with the air, this heat is largely utilized in producing water gas. The addition of this water gas to the producer gas, of course, considerably increases the fuel value of the latter.

285. Coal gas is made by the destructive distillation of soft coal. The coal is placed in fire-clay retorts or in ovens and heated to a white heat. The chemical compounds existing in the coal are mostly broken down and simpler substances are formed. Coke is left behind while a great variety of volatile substances, containing some of the carbon of the coal and all of the hydrogen, are driven off. After purification from tar, ammonia, sulphur compounds, etc., the gas is ready for delivery to the pipes of the city lighting system. This purification consists mainly in condensing all substances which, if not thus removed, would later condense when cooled in the gas mains, thus tending to clog them. It also serves to remove certain valuable by-products, principally coal tar and ammonia. The process in addition largely removes hydrogen-sulphide gas, the presence of which in the illuminating gas is objectionable, because on burning it produces sulphur-dioxide gas, which is harmful to people and to plants, especially when formed in poorly ventilated houses. The

condensation of the less volatile materials, such as tar, takes place in a series of condensers and scrubbers. The condensers may be either air or water cooled. In the scrubbers the gases are subjected to the cooling and dissolving action of water which is sprayed over a grid or lattice-like arrangement of wooden strips in a rectangular tower. The gases are thoroughly washed by contact with the large extent of wet surface. Thus much tar and ammonia are removed from the

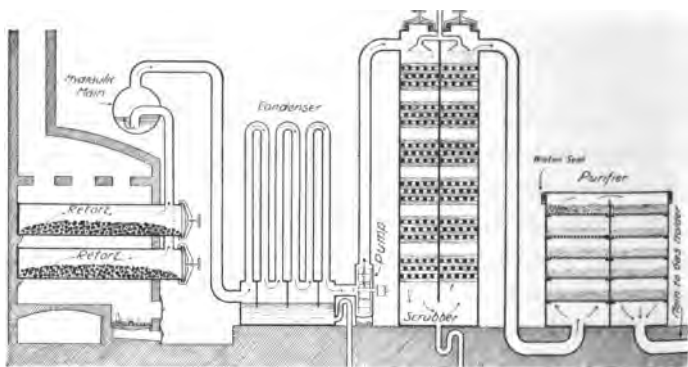


FIG. 57. — Manufacture of Coal Gas.

crude gas. Rotary scrubbers are also sometimes used in which the crude gas is churned with water to remove tar and ammonia and other objectionable materials.

The removal of the hydrogen sulphide is effected by means of iron rust, in the following fashion: iron turnings (to give great surface) are mixed with wood shavings (to keep the mass porous), and the mixture is then moistened and the iron allowed to rust. Large flat boxes (the purifiers) are packed with the mixture and sealed tightly by water seals. The gas is then led through the mass, when the hydrogen sulphide reacts with the hydrated iron oxide, iron

sulphide and water resulting. Thus the sulphur compound is removed from the gas. When the iron rust is spent, the mass is removed from the box and exposed to the action of the air, whereby the iron sulphide is oxidized and iron oxide is again obtained. The mixture can thus be used repeatedly until too full of the resulting uncombined sulphur for efficient results. Coal gas contains on an average nearly 50 per cent of hydrogen by volume, a considerable amount of methane, CH_4 , and smaller amounts of ethylene, C_2H_4 , acetylene, C_2H_2 , and many other compounds of carbon and hydrogen.

286. Luminosity of Flame. As a rule, hot gases are not of themselves luminous. Consequently, a flame which contains nothing but heated gases, as, for example, the hydrogen flame or the carbon monoxide flame, does not give off light.

On the other hand, the flame of burning ethylene, C_2H_4 , is brilliantly luminous. The light comes from solid particles of carbon raised to incandescence by the heat of the flame. On entering the hot zone, the gas is decomposed by the heat into hydrogen and free carbon. The hydrogen burns first with the limited supply of air that reaches the interior of the flame, while the minute particles of solid carbon remain suspended in the current of gas and give the light. As the white-hot carbon reaches the exterior of the flame, it comes in contact with oxygen and it too burns.

It is easy to prove that solid carbon exists in the interior of a luminous flame, for if a piece of cold porcelain is thrust into the flame, it becomes coated with soot (lampblack). The glowing particles of carbon are cooled by contact with the porcelain to below their kindling temperature before they get a chance to burn. (See Lampblack, Sec. 276.)

Ethylene is one of the typical *illuminants* of both water

and coal gas. It is obtained in water gas by the cracking of petroleum oil, whereas in coal gas it results naturally in small quantities from the decomposition of the coal. Another and more powerful illuminant that is present to some extent in water and coal gas is acetylene, C_2H_2 . The higher proportion of carbon which it contains is responsible in part for its high illuminating power. When pure acetylene is burned, it gives an extremely brilliant light.

287. Welsbach Mantles. One of the greatest inventions in the field of gas lighting is the Welsbach mantle. It is this mantle that is raised to incandescence by the heat of the flame rather than solid particles of carbon resulting from the decomposition of the gas itself. Where Welsbach mantles are used, it is a matter of indifference whether gas is rich in illuminants or not. Water gas can then be used without being enriched with "cracked" petroleum. The Welsbach mantles are composed of the oxides of two rare metals, thorium and cerium.

CARBIDES

288. Carbides. It has already been seen that the typically non-metallic elements, oxygen, chlorine, and sulphur, form compounds with the metals, that is, oxides, chlorides, and sulphides, respectively. Carbon is less distinctly a non-metal than the elements mentioned. It does not unite energetically with metallic elements, and the carbides when they are obtained are not as well-defined compounds as the oxides, chlorides, and sulphides. The carbides of iron, silicon, and calcium are worthy of mention on account of their importance in the industrial arts.

289. Iron Carbide. Molten iron is capable of dissolving a good deal of carbon in much the same manner as water

dissolves sugar. When the molten mass is allowed to cool very slowly, the carbon separates from its solution in the iron and appears partly as flakes of graphite and partly as microscopic crystals of a definite carbide of iron, Fe_3C . These flakes of graphite and crystals of iron carbide do not get a chance to settle out or to float off, but they remain suspended throughout the mass of metal to the etched surface of which they give a mottled appearance under the microscope.

If the melted iron is cooled very rapidly, none of the carbon has a chance to separate out, but it still remains in solution in the now solid iron (solid solution), and in consequence of the presence of carbon in this state the metal is extremely hard as well as brittle. The extreme hardness and brittleness may be removed to any desired extent by cautious reheating, — the so-called tempering process. During the tempering process more or less of the carbon passes from the solid solution into the microscopic crystals of iron carbide.

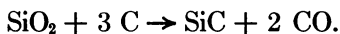
Iron carbide has never been prepared pure in large masses ; it is only known in the form of the infinitesimally small crystals embedded in masses of iron. It is, nevertheless, a substance of great importance in view of its pronounced effect upon the properties of iron and steel.

290. Silicon Carbide, SiC . This compound of carbon is of considerable practical importance on account of its extreme hardness,



FIG. 58. — Making Carborundum in an Electric Furnace.

which renders it of great value as a grinding material. It is known in the trade as carborundum. Grinding wheels, sharpening stones, etc., are made from powdered carborundum which is mixed with a binding material and molded into shape. Carborundum is made by heating quartz sand (SiO_2) with coke in an electric furnace. Part of the carbon withdraws oxygen from the silicon dioxide, while at the same time another part of the carbon unites with the silicon :



The carborundum is vaporized in the hottest part of the electric furnace, close to the coke core, and it crystallizes from

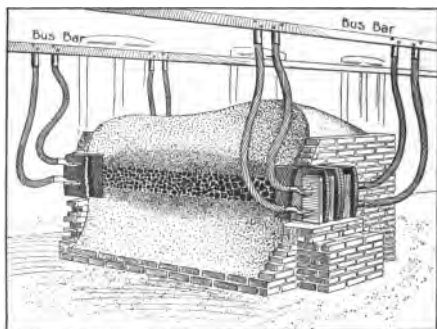


FIG. 59. — Section of Carborundum Furnace.

the state of vapor in the cooler regions around the core. The crystals are flat and thin and often-times are beautifully iridescent. They usually appear opaque because they contain traces of graphite, but the pure substance is

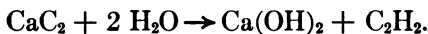
colorless and transparent. Carborundum is a very hard substance, — harder than any precious stone except the diamond. A crystal of carborundum will scratch glass with the greatest ease, but carborundum itself is easily scratched by the diamond.

291. Calcium Carbide is another important carbon compound, which, like carborundum, is made in the electric fur-

nace. The raw materials are lime and coke, which react according to the equation :



The calcium carbide thus formed is a hard, dark gray solid. The greatest value of calcium carbide depends upon the fact that it reacts with water to form acetylene gas :

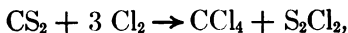


COMPOUNDS WITH NON-METALS

292. In the carbides, carbon plays the part of a non-metallic or electro-negative element. When, however, carbon combines with the more active non-metallic elements, it becomes forced to take up the electro-positive rôle itself and thus we have carbon oxide as well as carbon sulphide and carbon chloride.

293. Carbon disulphide, CS_2 , is made by the direct union of carbon and sulphur vapor at a high temperature. It is a colorless volatile liquid which is much used as a solvent in rubber cements. It also dissolves fats, waxes, iodine, sulphur, and many other substances which do not dissolve in water. Hence its greatest use is as a solvent. It is also used to exterminate insect pests which infest grain, and to kill ants. It should be used with caution for these purposes, for inhaling its vapor is injurious and may even prove fatal.

294. Carbon tetrachloride, CCl_4 , is a colorless liquid which, like carbon disulphide, finds its principal use as a solvent. It has an advantage over the latter in that it is non-inflammable, and it is not so volatile. It is usually made by treating carbon disulphide with chlorine,



and distilling it off from the resulting mixture. Large quantities are now sold under various fanciful names as a cleansing fluid for removing grease spots. Being non-inflammable, it is safer than benzine and gasoline. Other large amounts are sold for use in fire extinguishers. These are especially efficient in putting out gasoline fires. The vapor of carbon tetrachloride is not only non-inflammable, but it is also very heavy and hangs over the fire and smothers it.

SUMMARY

Free carbon exists in three forms: (1) amorphous carbon (coke, charcoal, lampblack, gas carbon, coal); (2) graphite; (3) diamond. Amorphous carbon is without definite form. Graphite forms hexagonal crystals. Diamond crystallizes in the regular system. Graphite is one of the softest solid substances. Diamond is the hardest substance known. Graphite, diamond, and amorphous carbon all burn in oxygen and yield only carbon dioxide. The differences between amorphous carbon, graphite, and diamond are believed to be due to a difference in molecular structure.

Carbon dioxide is the product of the free combustion of carbon; it is stored in vast quantities in nature in the form of carbonates.

Carbon monoxide is a valuable fuel. It is largely present in water gas and in producer gas.

Water gas is made by blowing steam through white-hot coke.

Producer gas is made by blowing air through a deep bed of hot coal or coke.

Coal gas is made by the destructive distillation of soft coal in retorts.

The luminosity of flames is due to the presence in them of heated solid particles, usually of carbon.

Carbides: Carbon is not a very active non-metal, hence the carbides of the metals are not as easily formed as the oxides, chlorides, and sulphides.

Iron carbide is exceedingly important because of the effect of its presence upon the properties of iron and steel.

Silicon carbide (carborundum) is a very useful artificial abrasive.

Calcium carbide is important as a source of acetylene.

Carbon disulphide and carbon tetrachloride are compounds of carbon with non-metals. Their chief value is due to their solvent powers.

Questions

1. What is the most valuable form of carbon? What is the most useful form?

2. Of what substance are the "leads" of lead pencils made? How is the hardness of pencils varied?

3. Why is graphite used on bicycle chains?

4. How may diamonds be made artificially?

5. How is graphite made artificially?

6. Why does not pure water gas give a luminous flame? How may it be made to do so?

7. Explain the function of the "generator," the "carburetor" and the "superheater" in the production of water gas as shown in Fig. 55. Explain the operation of the valves.

8. How is producer gas made? Explain the diagram, Fig. 56. What is the service performed by the economizer? What is the object of allowing water to trickle into the economizer?

9. How is coal gas made? Explain the diagram, Fig. 57.

10. Which would give the hotter flame, producer gas or water gas? Why?

11. How is carborundum made?

12. How is calcium carbide made?

13. What are the principal uses of carbon tetrachloride? What advantage has it over carbon disulphide?

CHAPTER XXIV

COMPOUNDS OF CARBON (*Continued*)

295. Organic Chemistry. The compounds of carbon are studied under a special division of chemistry known as *organic chemistry*; the original significance of the name was that these compounds were produced by the life processes of plants or animals, that is, of living *organisms*. Some compounds, it is true, which were considered organic were formed by the partial decomposition of compounds produced by living organisms rather than formed directly by the organisms themselves.

As examples of the type of substances formed directly in living organisms, we have starch and sugar. Starch is formed in potatoes, in grains, and in many other kinds of plants. Sugar is formed in the sugar cane, the sugar maple, and the sugar beet. Acetic acid, methyl alcohol, and acetone are examples of organic substances produced indirectly from others which were formed by living organisms. These three substances result when wood is destructively distilled. Benzene, carbolic acid, naphthalene, and methane are organic substances obtained by the destructive distillation of soft coal (coal being the product of the partial decomposition of woody material which grew in some past geologic age). As examples of organic substances produced by the growth of animals, we have the various protein substances such as egg albumin (the white of egg is mainly albumin and water) and gelatin (which is extracted from bones and hides by boiling).

Formerly it was supposed that the mysterious agency of life was essential to the formation of organic compounds, but one by one the organic compounds have been synthesized in the laboratory until now all but the most complicated can be built up by strictly inorganic agencies from their elements, these elements being carbon and usually hydrogen, with oxygen and nitrogen often, and sulphur, phosphorus, and iron sometimes, in addition.

Thus there is really no hard and fast line between organic and inorganic chemistry. The compounds of carbon are so numerous and the chemistry of these compounds so complicated that it is more convenient to separate this field of chemistry from the inorganic field for the purpose of study.

As was suggested above, it was once thought that organic compounds could be produced only by the agency of vital force. To-day it is recognized that chemical reactions, which are in every way analogous to the reactions which take place in laboratory test tubes, take place within animal and plant tissues and that the life and growth of the organisms depend on the chemical changes rather than that the chemical changes depend on the vital force.

In our study of inorganic chemistry, we have observed that compounds are always possible between metals and non-metals, or, in other words, between electro-positive and electro-negative elements. Now carbon is neither a distinct metal nor a distinct non-metal, and in its ability to form compounds it shows itself markedly different from other elements. Its valence in its compounds is four, and the most striking feature about its combining relations is that it is apparently a matter of indifference whether these four valences are exerted in holding positive or negative elements or whether

they are divided, part holding positive and the rest holding negative elements. Moreover, carbon possesses a peculiar ability to use a part of its valences in uniting with other carbon, while at the same time the rest of its valences are exerted in holding other elements. On this account, a vastly increased number of compounds of carbon is possible.

Among the possible compounds, thousands of actual ones are known, and in this brief chapter on organic compounds a few only of the more interesting of the carbon compounds can be considered. Compounds consisting only of carbon and hydrogen (called *hydrocarbons*) form a large and important group.

METHANE AND THE PARAFFIN SERIES

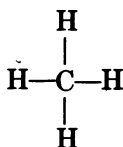
296. Methane, marsh gas, CH_4 , is the simplest member of an extended series of organic compounds. The gas which arises when one pokes a stick into the mud beneath the pools of water in marshes consists mainly of this substance. In addition to being formed in the mud of marshes, methane is also frequently present in coal mines, resulting from the decomposition of coal, and its presence is the cause of many serious explosions. The coal miners call it *fire damp*. It is also a very important constituent of the illuminating gas that is obtained by the destructive distillation of coal, and large amounts of it are present in natural gas.

Carbon tetrachloride is of interest in its relation to methane. In methane the carbon atom has attached to it four positive hydrogen atoms, whereas in carbon tetrachloride the place of the hydrogen is taken by four electro-negative chlorine atoms.

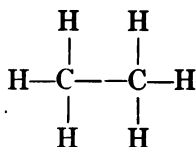
Compounds with the formulas, CH_3Cl , CH_2Cl_2 , and CHCl_3 , are also known. The last is the well-known substance chloro-

form. In these compounds carbon is united with both positive and negative elements. Not only is it possible to replace one or all of the hydrogen atoms of methane with chlorine, but also with other atoms or groups of atoms.

297. The Paraffin Series. A compound is known, which may be regarded as methane in which one hydrogen atom has been replaced by the group CH_3 . This new compound is called ethane. Here, carbon may be considered as united with itself as well as with an electro-positive element, hydrogen.



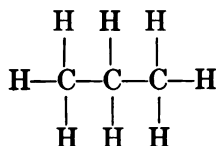
Methane



Ethane

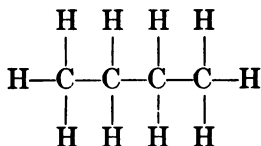
Ethane, like methane, is found in illuminating gas made by the destructive distillation of soft coal.

By displacing an atom of hydrogen from ethane by means of the CH_3 group, a new compound known as propane results.



Propane

By replacing an atom of hydrogen of propane by a CH_3 group, butane is obtained.



Butane

Butane is one of the more volatile components of petroleum. Petroleum, which is a crude, offensive oil drawn from the earth in various localities, is in the main a mixture of many hydrocarbon compounds belonging to the series whose first few members have just been mentioned. In this series with the introduction of each new CH_2 group, the molecular weight, of course, increases, and it is interesting to note that the boiling points of the successive substances increase in a somewhat regular fashion. Other properties, such as specific gravity, for example, also vary with varying molecular weight. The higher the molecular weight, the denser the substance becomes.

298. Distillation of Petroleum. In separating the great mixture of hydrocarbons, known as crude petroleum, advantage is taken of the variation in boiling points, and by distilling off fractions of the whole into separate containers, the crude mixture is separated into portions of varying volatility, the most volatile portions being first to come off. Petroleum contains so many different members of the paraffin series, and the molecular weights and hence the boiling points are so near to each other, that it is not practically possible by distillation to obtain one of the pure substances entirely by itself.

The first fractions containing several of the more volatile members of the paraffin series are condensed and sold under the trade names of cymogene and rhigolene. These are very volatile liquids, and they are sometimes used to chill portions of the body surface to deaden sensation during minor surgical operations. The rapid evaporation of the very volatile liquid takes up the heat of the part sprayed with it, thus chilling the flesh and causing it to become numb. The later and less volatile fractions from petro-

leum are called successively gasoline, naphtha, benzine (not benzene) and kerosene.

After the kerosene is distilled off, there remains still a mixture of many of the higher hydrocarbons of the paraffin series from which heavier oils are distilled. When these oils are chilled, flakes of paraffin separate. This is removed by filter pressing and the oil is used for lubricants. The viscous substance known as vaseline is obtained from the residue left when the crude oil is distilled in a vacuum.

The last volatile fractions of the petroleum come off only when the bottom of the still has risen to a red heat; and the residue then left in the still is coke in a form which is highly valued for making electric light carbons.

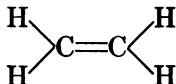
All of these substances obtained from petroleum are very resistant to attack by chemicals except at high temperatures. Hence the origin of the name of the series, paraffin, suggesting lack of affinity.

UNSATURATED HYDROCARBONS

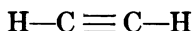
299. A number of other natural series of hydrocarbons are known, the ethylene series in which the first member is ethylene, C_2H_4 , and the acetylene series in which acetylene, C_2H_2 , is the first member, being among the more important. The relation between molecular weights and properties which was noted in the paraffin series is found also in the other series of hydrocarbons.

In ethylene and acetylene it is believed that carbon still possesses its universal valence of four, but in order to maintain this belief, it becomes necessary to suppose that more than a single valence of one carbon atom is employed in holding

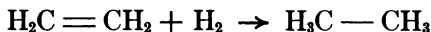
an adjacent carbon atom. Thus ethylene is supposed to possess a *double bond*



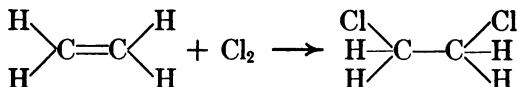
and acetylene a *triple bond*



The justification of the term *unsaturated* in describing compounds of this character lies in the fact that they are literally unsaturated. For example, ethylene, when mixed with hydrogen and passed through a heated tube containing a suitable catalyzer, takes up additional hydrogen easily and is changed into ethane, a saturated compound



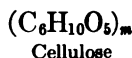
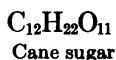
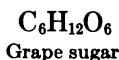
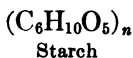
or, treated with chlorine, ethylene readily changes into dichlor-ethane.



As already indicated in the preceding chapter, ethylene is an important constituent of illuminating gas, and acetylene finds extensive use as an illuminant, as in automobile headlights.

CARBOHYDRATES

300. There is another great class of carbon compounds, known as carbohydrates, in which hydrogen and oxygen in precisely the right proportion to form water are united with carbon. Starch, sugars, gums, and cellulose are carbohydrates. The formulas of a few of the many carbohydrates are as follows :



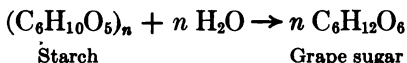
It is seen that starch and cellulose have the same formula with the exception of the subscripts m and n . These subscripts m and n signify some definite but unknown numbers, probably large and probably different.

301. Sugars. Sugars are found in nature in the sap of plants and the juices of fruits. The sugars are built in the leaves of plants by the interaction of the carbon dioxide of the air and the water of the sap under the influence of sunlight and the chlorophyll, or green coloring matter of the leaves. The energy of the sunlight is consumed in splitting up the carbon dioxide so that oxygen is returned to the air, while the carbon and water unite, forming carbohydrates.

The sugars, which are soluble in water, are conveyed by the sap to all parts of the plant and are converted into starch, or cellulose, or other sugars by the chemical addition or subtraction of water as the needs of the plant may require.

Cane sugar is the variety of sugar found in the sap of the sugar cane, the sugar beet, and the maple tree.

Grape sugar is found in grapes and other fruits. It is less sweet than cane sugar. Starch can be converted artificially into grape sugar by boiling with dilute acids, this treatment promoting the addition of water according to the equation



Enormous quantities of corn starch are thus treated in making commercial glucose, a product which consists mainly of grape sugar and dextrin (see below), the latter being an intermediate product between starch and grape sugar. Commercial glucose is ordinarily a thick sirupy product and is often sold for table use under the name of corn sirup. Evaporated to dryness, it yields solid "grape sugar."

302. Starch is insoluble in water and it is the form in which carbohydrates are stored up by plants for their future use as foods. It is thus found especially in bulbs, tubers, and seeds, where it is accumulated for the nutrition of the young plants.

Potatoes are composed almost wholly of starch and water. Wheat, rice, barley, corn, and, in fact, all grains are composed largely of starch. Consequently, the food value to man as well as to the plants themselves, of all kinds of grains, tubers, bulbs, etc., is largely due to their content of starch.

Starch before it is assimilated in the human body is converted back to soluble sugars by the action of the digestive juices.

Starch is always found in plants in the form of small compact granules, and it is usually possible to determine the source of any particular starch by a microscopic examination of the starch granules.

Dextrin, which is the adhesive substance with which the backs of postage stamps are coated, is an intermediate product between starch and sugar, and it is obtained by heating starch. Dextrin is formed to some extent in baking bread, and it is present in the browned crust.

303. Cellulose is the chemical substance of which the fibrous and woody part of plants is composed. It is not used as food by man (except in small quantities in the tender green leaves of lettuce, spinach, etc.), but it finds enormous use in the textile industries and in paper making. Cotton, linen, and wood fiber, for example, are almost pure cellulose.

Wood consists of bundles of cellulose fibers cemented together with resinous or gummy material. Although old linen rags furnish the cellulose fiber for some of the strongest grades of paper, the principal source of the cellulose is wood.

The fibers are sometimes torn apart mechanically for the cheapest paper, but usually wood chips are treated chemically to dissolve out the binding material and thus leave the pure cellulose as a loose mass of fibers.

The paper used in the laboratory for making filters is practically pure cellulose. Other grades of paper are likely to be filled with mineral matter to give weight, or with glue or casein to give a hard, smooth finish.

ALCOHOLS

304. Alcohol, C_2H_5OH , is prepared by the action of yeast, a microscopic plant cell, upon grape sugar, or other type of sugar. These little plants consume a great deal of sugar in their life process, and they increase in numbers with astonishing rapidity when placed in a favorable medium. The reaction brought about by the yeast plants is approximately expressed by the equation



Heat is evolved in this reaction, and carbon dioxide is formed as well as alcohol. Since most of the sugar thus fermented in the commercial preparation of alcohol is derived from the starch of grains, this kind of alcohol is known as grain alcohol, to distinguish it from other alcohols.

When, in the fermentation of the grain, the alcohol reaches a concentration of 10 to 12 per cent, the action becomes very slow and almost ceases. By fractional distillation, the alcohol is now separated from the water and the solid residue, so that a 95 per cent alcohol is obtained in the distillate.

The distillation of alcohol is an important industry, since alcohol finds many uses in the arts, — as a fuel, as a solvent,

and in many other ways. Large quantities of it are consumed in a more or less diluted condition in spirituous and fermented liquors.

From the standpoint of chemistry as well as from that of economics, the use of alcohol in beverages is wasteful. In fermenting the sugars much energy is lost as heat, and much labor that might be used productively is required to care for the process. The distillation, also, requires much heat, energy, and labor, and the products are stored for long periods, thus keeping much capital idle.

From the physiological standpoint alcohol is a powerful poison. Although it has been shown by scientists that alcohol is burned in the body and furnishes heat and energy like the carbohydrates, nevertheless alcohol has very harmful effects upon the nervous system and through that upon the processes of assimilation of food. Pure alcohol is a deadly poison; somewhat diluted, as in whiskey, rum, and brandy, it is very harmful; and more highly diluted, as in fermented beverages, it is injurious and its use is not advisable.

305. Denatured Alcohol. On account of the far-reaching evil effects of the use of alcohol as a beverage governments have frequently placed heavy internal revenue taxes upon the traffic in alcohol, thus limiting its use and at the same time raising revenue for governmental expenses.

The resulting high price of alcohol has in times past limited its use as a fuel and as a solvent in the arts and industries. Recently the United States government has permitted the sale without tax of alcohol which has been "denatured," as it is called, by the addition of certain other substances. The object of this addition is to render the alcohol unfit for use as a beverage without in any way harming it for industrial purposes. Various substances, among them pyri-

dine, may be used to denature alcohol. A substance with an evil odor is usually employed so as to render the mixture offensive to drink.

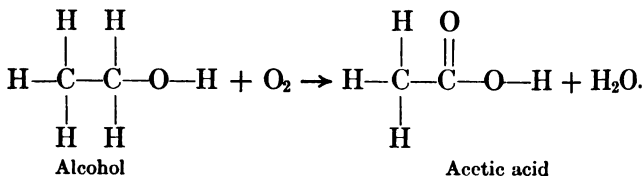
306. Wood Alcohol, CH_3OH , is obtained by the destructive distillation of wood. Wood alcohol is very similar to grain alcohol in its properties and these two alcohols can be used almost interchangeably for fuel and solvent purposes. It should never be used as a constituent of beverages, because, although its poisonous properties are of the same general character as those of grain alcohol, it is a so much more violent poison that its use is likely to prove immediately fatal. The vapor even is dangerous if inhaled in quantity, and its action upon the eyes is likely to cause blindness.

ORGANIC ACIDS

307. Organic acids are found in many fruits, notably citric acid in the lemon, orange, and other citrus fruits, malic acid in the apple, and the acid salt of tartaric acid (cream of tartar) in grapes. In addition to these natural fruit acids there are a great many acids which are formed by the partial oxidation of organic substances like the alcohols and sugars. Organic acids are, as a rule, very weak as compared with the mineral acids, hydrochloric, nitric, and sulphuric. Like the carbohydrates, they are oxidizable in the body; hence their desirability in foods to which they impart a mild and pleasing sour taste.

308. Acetic acid, $\text{H}(\text{C}_2\text{H}_3\text{O}_2)$, perhaps ranks first in importance among the organic acids. It is the acid of vinegar. Cider is the product of the alcoholic fermentation of apple juice. By allowing cider or other fermented liquor of similar alcohol content to undergo a different sort of

fermentation under the influence of certain bacteria, in the presence of air, an oxidation of the alcohol to acetic acid takes place.



For industrial uses, acetic acid is made by the destructive distillation of wood. The cellulose is not completely decomposed by the heat, but it is broken down into a great variety of volatile organic substances, which distill off, and charcoal, which remains in the retort. Wood alcohol, as already mentioned, is one important product of the distillation; acetic acid is another.

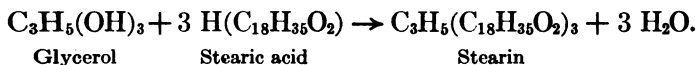
It should be noted that although practically all organic compounds contain hydrogen, not all are acids. Even in acetic acid, only one of the hydrogens functions as acid hydrogen. Hence in the formula, $\text{H}(\text{C}_2\text{H}_3\text{O}_2)$, a single hydrogen is placed alone, whereas the other three are placed with the acid radical ($\text{C}_2\text{H}_3\text{O}_2$).

FATS

309. Fats are compounds of carbon, hydrogen, and oxygen, and they may be regarded as a product of the union of certain higher alcohols with certain higher acids; called fatty acids, much as salts are the product of the union of bases and acids. Instead of acting instantly with acids, as do bases, the alcohols react very slowly.

Stearin is the principal fat in tallow and is represented by the formula $\text{C}_3\text{H}_5(\text{C}_{18}\text{H}_{35}\text{O}_2)_3$. It is derived from glycerol,

$C_3H_5(OH)_3$, an alcohol with three hydroxyl groups, and stearic acid, $H(C_{18}H_{35}O_2)$. Three molecules of stearic acid are necessary to unite with glycerol according to the equation

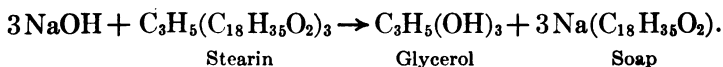


The equation is similar to that of a neutralization reaction, but it should be remembered that the glycerol is not perceptibly a base and such a reaction can be carried out only with difficulty in the laboratory. Fats are formed mainly in the slow chemical processes taking place in animal and plant tissues.

The reaction represented by the reverse of the above equation can take place rather easily, and fats on standing often become rancid, due in large part to the separation in this manner of the free fatty acid. This action is known as hydrolysis.

Fats are valuable foods; they yield nearly two and one quarter times as much heat when oxidized in the body as carbohydrates or proteins. They are thus splendid food for cold weather or cold climates, but they are somewhat difficult of digestion. Broadly speaking, all fats and oils obtained from animals and plants, including butter, lard, olive oil, cottonseed oil, and castor oil, are similar chemically to stearin.

310. Soaps are made by the action of strong mineral bases upon fats. For example, when sodium hydroxide acts upon stearin, glycerol is separated from the fat and sodium stearate, a salt of the organic acid, is formed.



Sodium stearate is a typical soap.

PROTEINS

311. The albumin of the white of eggs is one of a number of carbon compounds which may be classed together under the name of proteins. The proteins contain carbon, hydrogen, oxygen, and nitrogen always, and they may contain small amounts of other elements, as phosphorus, sulphur, and iron. To this class of carbon compounds belong the tissue-building foods such as are found in greatest abundance in meat, milk, eggs, cheese, the gluten of wheat, beans, and peas. It was said in Chapter VII (while discussing the fixation of atmospheric nitrogen) that legumes were able, by the aid of bacteria living on their roots, to cause the free nitrogen of the air to combine with other elements to form nitrogenous compounds. These compounds become stored up as proteins principally in the seeds of the leguminous plants. The animal foods — meat, milk, eggs, and cheese — contain proteins derived from the plant food eaten by the animals. Animals possess the power to make over many protein substances into other proteins which are better adapted to the needs of the particular organism, but animals do not themselves seem to be able to put together the elementary substances to form the proteins.

SUMMARY

Many of the compounds of carbon, which it was formerly supposed could only be formed in living organisms, can to-day be prepared in the laboratory.

The valence of carbon is four. These valences may be exercised in holding electro-positive or electro-negative elements or part of both at the same time. Some of the carbon valences may also hold other carbon atoms. Many thousands of different compounds of carbon are known.

Methane is the first member of a series of hydrocarbons called the paraffin series. Ethane, propane, and butane are the next three

members of this series. Methane is one of the products formed when organic substances decompose without a free supply of air. It is found in coal mines, and the gas from marshes is mainly methane. Natural gas also contains methane.

Carbon tetrachloride is a useful solvent. Its composition shows that it may be regarded as a derivative of methane. In it the carbon is united to an electro-negative element.

The paraffin series illustrates the remarkable relation between molecular weights and properties in an homologous series.

Petroleum oil consists mainly of various members of the paraffin series. It may be roughly separated by fractional distillation into the various commercial products of petroleum.

Ethylene and acetylene are the first members of two unsaturated series of hydrocarbons.

Carbohydrates are a very important class of carbon compounds. Many of our most valuable foods are carbohydrates, as, for example, sugar and starch. Dextrin and cellulose also are carbohydrates.

Alcohol is another carbon compound of considerable use in the arts. It is also used in many beverages, but such use is both uneconomical and unwise from the standpoint of health. Wood alcohol is chemically similar to grain alcohol. It is far more poisonous.

Organic acids are found in many fruits. They are far weaker than the mineral acids H_2SO_4 , HCl , and HNO_3 . Some organic acids are derived from the oxidation of alcohols or sugars by fermentation. Acetic acid, the acid of vinegar, is the principal one of these. Acetic acid is also obtained by the destructive distillation of wood.

Fats are valuable foods. They are formed from alcohols and organic acids. They may hydrolyze, whereby the fatty acid is set free. Soap is the sodium salt of some of the fatty acids of common fats. Glycerol is a by-product of the soap industry.

The proteins are organic compounds containing nitrogen, and they are valuable foods. Plants form proteins directly from the simpler substances, but animals only remake proteins from other proteins obtained from plants.

Questions

1. Why is organic chemistry usually studied apart from inorganic chemistry?
2. Is there any real difference between the two branches of chemistry?
3. What peculiarity in combining ability distinguishes carbon from other elements?
4. What has this peculiarity to do with the existence of a vast number of organic compounds?
5. Any member of the paraffin series may be represented by the general formula $C_nH_{(2n+2)}$. What, then, is the formula of that member of the series which has 18 carbon atoms? 10 carbon atoms? 5 carbon atoms?
6. How is gasoline obtained from crude petroleum?
7. What peculiarity of composition distinguishes the carbohydrates?
8. What is grape sugar commonly called?
9. What weight of alcohol might be obtained by the complete transformation of 100 grams of glucose? (See equation on page 291.)
10. Why is the use of alcohol as a beverage uneconomical, aside from its harmful effect?

CHAPTER XXV

THE IONIC THEORY

312. Electrical Conditions of Acid Hydrogen. It was shown in Chapter XIX that the characteristic properties of acids must be attributed to the presence in them of hydrogen which is in a different state of combination from ordinary combined hydrogen and which has been designated as displaceable or acid hydrogen.

The acid properties of the hydrogen in acids are not manifest when the acid is pure and dry, but are developed when the acid is dissolved in water. It is now generally believed that the solvent in some way separates the molecules of acid into two components, of which one is the hydrogen atom (or atoms in acids like H_2SO_4 and H_3PO_4) and the other is the acid radical. Furthermore, it is believed that the hydrogen atom so separated is charged with positive electricity and the acid radical is charged with negative electricity. These electrically charged components of the acid are known as *ions*. According to this supposition, the hydrogen ion is a component of every acid solution, and it is the one which produces the acid properties.

313. Electrostatic Attraction and Repulsion. It is a well-known fact that when the hair is combed on a cold, dry day the hair stands on end as if the separate hairs repelled each other, but that the hairs are all attracted to the comb. The friction of the comb on hair leaves the latter charged with

positive electricity and the former with negative electricity. This simple experiment illustrates a general law of electricity, that like charges repel and unlike charges attract each other.

The electricity that is available in the laboratory for chemical work is generated either chemically in electro-chemical cells, or mechanically by dynamos in which coils of wire are rotated in magnetic fields, but scarcely ever by friction.

314. Electricity is something very intangible. We do not feel like calling it a substance, for it does not seem to have weight. It probably pervades all ordinary substances, and yet its presence is commonly unnoticed. We are not ordinarily conscious on a windless day that we are living at the bottom of a sea of air which presses heavily upon us and everything around us. But we become conscious of the presence of the air when it is in motion, as when the wind blows, or when it is compressed as in an automobile tire, or when it is rarefied, as in an electric light bulb, which collapses with a loud report when it is broken. In these respects, electricity is not very unlike air. Friction may be supposed to act in a measure like an air pump and to withdraw electricity from one object and compress it into another. If positive electricity is at a higher pressure in the hair than in the surroundings, it makes itself obvious, and we see the hair stand on end as a result. Similarly, if negative electricity is at a higher pressure on the rubber comb than in surrounding objects, it again makes that fact obvious by its ability to attract the positively electrified hair. Air can be forced by a pump through a pipe and at the end of the pipe be made to do work, as in running a compressed air drill. Likewise, electricity may be forced by an electric pump, — that is, a dynamo, or an electro-chemical cell, — to flow through a circuit and to do work as in running a motor or in decomposing a

chemical compound like sodium chloride into its constituent elements.

315. Metallic Conduction. It is a matter of common knowledge that metals are invariably used to conduct electric currents, and that non-metallic substances, such as glass, rubber, and sulphur, are used as insulators. Electricity passes with great ease through metals, in fact, its flow through metals can be likened to the flow of water through pipes. So far as we can detect, the metal suffers no more alteration by the passage of the current than the pipe suffers by the passage of water.

316. Non-Conductors. Substances other than metals ordinarily offer great resistance to the passage of electricity, and on this account are termed non-conductors. Non-metallic substances include not only the non-metallic elements themselves, but also compounds, even compounds containing metals. For example, sodium chloride possesses none of the characteristics of metals

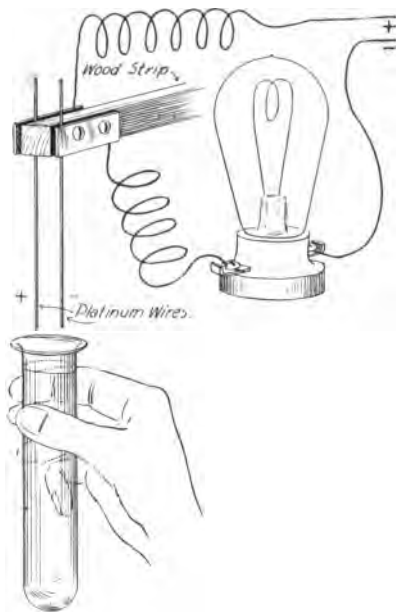


FIG. 60. — Apparatus for showing Electrical Conductivity. The brilliancy with which the lamp glows is a measure of the conductivity of the substance placed between the electrodes.

and when it is dry it does not conduct electricity. Water is another distinctly non-metallic substance and, like the

other substances in its class, it is when pure an almost complete non-conductor of electricity.

317. Electrolytic Conduction. We now come to a most remarkable series of phenomena. Water as stated does not conduct electricity when pure, no more does dry sodium chloride; but dissolve sodium chloride in water, and a solution is obtained which conducts the current readily.

This may be strikingly shown if an electric circuit is arranged as shown in Fig. 60. Connections are made at the points marked + and - with the two wires of the 110-volt direct-current incandescent lighting system. Alternating current will serve equally well. Between these two connections there are inserted in the circuit an incandescent lamp and a gap between two platinum wires (electrodes). These wires are suspended from binding clamps, parallel and near to each other, but not touching. The circuit as now arranged passes through the incandescent lamp but is broken by the gap between the platinum electrodes. If these are connected by a piece of metal, the circuit is completed and the lamp glows with its full brilliancy. If a piece of non-conducting substance is held so as to touch both electrodes, no current passes and the lamp does not glow.

On holding a dry lump of common salt so that it touches both platinum electrodes, the lamp does not glow and the salt is thus shown to be a non-conductor. On raising a small vessel filled with distilled water from underneath so that both electrodes dip in the liquid, no light is seen in the lamp, and water is also shown to be a non-conductor. If, now, a little of the salt is dissolved in the water and the conductivity of the solution is tested in the same way, the lamp is seen to glow brilliantly, and the solution of sodium chloride is proved to be a good conductor.

318. Not only does a solution of sodium chloride conduct strongly, but solutions of all *salts* conduct in about the same degree. Hydrochloric and sulphuric acids, which we have spoken of as *strong* acids, likewise cause the lamp to glow brightly when their solutions are placed between the platinum wires; phosphoric and acetic acids, which are known to be weaker acids, cause the lamp to glow with a dull red, showing that these acids conduct, but to a much smaller extent than the strong acids; carbonic acid, which we know as a very weak acid, does not conduct sufficiently to cause the lamp to glow, but still it does conduct to some extent, as could be shown with a more delicate instrument for measuring the passage of the electric current. Solutions of the strong bases, sodium hydroxide and potassium hydroxide, give a brilliant glow to the lamp, showing that they conduct the current to about the same degree as solutions of salts and of strong acids. A solution of the weak base ammonium hydroxide gives a dull red glow to the filament, and thus conducts to about the same extent as the weaker acids.

319. Non-Electrolytes. Solutions of some substances, for example sugar and alcohol, do not conduct any better than pure water. Such substances are called *non-electrolytes*, in distinction to *electrolytes* which do conduct when dissolved.

320. Character of Electrolytic Conduction. All dry, solid salts are like dry sodium chloride in that they do not conduct electricity. Pure acids and pure bases when entirely free from water are also non-conductors. All become conductors when they are dissolved in water, but the manner in which the conduction takes place differs strikingly from the manner in which it takes place in metals. In metals, absolutely no permanent change takes place in the conductor, but in solutions the passage of the current is accompanied

by a decomposition of either the dissolved substance or the water. The passage of electricity through a solution together with the accompanying decomposition is known as *electrolysis*, a term which we have already used a few times.

321. The Ionic Theory. It was in the effort to explain the remarkable facts concerning electrolytic conduction that the theory of ions was developed. The theory in its present form was proposed by Arrhenius, a Swedish physicist, in 1887, and was called by him the *electrolytic dissociation theory*; it is now more commonly known as the *ionic theory*.

According to the ionic theory, when a salt — or acid, or base — is dissolved in water, its molecules become *dissociated*, or separated, into two components called *ions*. These ions are heavily charged with positive and negative electricity, respectively. The process of ionization may be represented by an equation in the same manner as an ordinary chemical reaction, for example the ionization of sodium chloride takes place as follows:



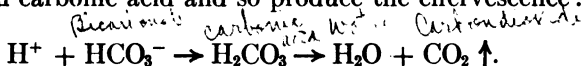
The electric charges are represented by the symbols⁺ and ⁻.

322. Pairing of Ions. The ions are separated by the action of the water so that they are free to move about in the solution to some extent independent of each other; but, of course, the attraction between the unlike charges of electricity is so great that a positive ion cannot be drawn away from the immediate neighborhood of its accompanying negative ion unless there is another negative ion near which will attract it, while at the same time there is another positive ion near to attract the now unbalanced negative ion. This amounts to saying that every positive ion must at all times be paired off with a negative ion, but that the attachment of the ions in the pair is not

so firm as to prevent a continual interchange of partners, so to speak.

323. Reactivity of Ionized Substances. In non-ionized substances, we may suppose, if we like, that the two components still possess the electric charges, but that, without the action of water to separate the components, they remain so firmly bound together in the molecule that this interchange of partners is not possible.

It is a well-known fact that dry, solid substances are inactive when cold. For example, baking powder, which is a mixture of a dry powdered acid substance with dry sodium bicarbonate, remains without action indefinitely so long as it is kept dry. When it is moistened, on the other hand, it reacts immediately. The acid substance dissolving in the water gives H^+ ions and the sodium bicarbonate gives HCO_3^- ions. These ions enter immediately into reaction, leaving their former partners and pairing with each other, whereby they form carbonic acid and so produce the effervescence:



324. Electrolytic Conduction. When an electric current passes through a solution, it does not pass in a continuous stream, as water through a pipe, but it travels only upon the ions, which act as carriers. Each ion bears a definite load of electricity, the positive ion a load of positive electricity which it carries through the solution to the negative electrode, and the negative ion a load of negative electricity which it carries to the positive electrode.

325. Degree of Ionization. Some substances in solution conduct electricity strongly. It seems fair to assume that these substances have yielded a large number of carriers, that is, of ions. As a matter of fact, there are good reasons for

believing that salts and strong acids and strong bases do yield a large number of ions when dissolved; the great majority of the molecules are dissociated. On the other hand, only a small proportion of the molecules in the weak acids and bases are split up into ions; the rest of the molecules remain undissociated and incapable of taking part in the conduction of electricity. Thus in a solution of acetic acid, which we have said is a weak acid, it is estimated that about one molecule in every one hundred is dissociated, whereas the other ninety-nine molecules are intact. We attribute acid properties to the presence of hydrogen ions, and it may be seen that according to the theory the weakness of the acid character of acetic acid and the feebleness of its conductance arise from the same cause, namely, from a disinclination or inability of its molecules to break apart into ions.

326. Value of Ionic Theory. When Arrhenius originated the ionic theory, he was led to his conclusions, not only by the phenomena of conduction and by the similarity of properties of all acids and of all bases, but also by a number of other striking properties of conducting solutions. It is beyond the scope of this book to give all of the reasons for adopting the ionic theory; but it may be said that it is believed to-day by most chemists that the ionic theory gives a reasonably correct picture of the conditions in solutions that conduct electricity. Without this theory it would be difficult to account for electrolytic conduction or for the fact that all acids have the same acid properties and all bases have the same basic properties. We make use of the ionic theory because it is a great aid in helping us to understand chemical principles and to systematize our knowledge of the chemistry of solutions.

327. Neutralization According to Ionic Theory. One of the greatest services of the ionic theory is that it has given us

a far clearer understanding of neutralization reactions. We have said that the neutralization of an acid and a base results in the formation of water and a salt with a disappearance of the characteristic properties of acid and base. According to the ionic theory an acid when in solution consists of a hydrogen ion and a radical ion and a base consists of a metal ion and an hydroxyl ion. Thus hydrochloric acid is



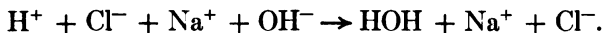
and sodium hydroxide is



Pure water does not conduct electricity and therefore does not contain ions but only molecules of H_2O (or HOH). Now on bringing acid and base together, H^+ ions and OH^- ions come into contact. They are components of water, but water cannot exist in ionized form; in other words, these components cannot continue to exist separately when in presence of each other, they combine to form undissociated water molecules,

$$\text{H}^+ + \text{OH}^- \rightarrow (\text{HOH}) \text{ or } \text{H}_2\text{O}.$$

Sodium chloride, on the other hand, we know to exist in solution in the form of ions. Hence the Cl^- ion of the acid and the Na^+ ion of the base do not suffer any change during the neutralization but simply *remain* in the neutralized solution. The complete neutralization reaction would thus appear as follows:



The resulting solution is identical with one that would be obtained by dissolving solid sodium chloride in water, hence we are perfectly correct in speaking of it as a sodium chloride solution. If this solution is evaporated, water escapes as water vapor and the Na^+ ions and Cl^- ions, no longer being

held apart by the water, join to form molecules of sodium chloride. When the water is all evaporated, nothing is left but solid sodium chloride.

It is thus true that water and a salt are the products of neutralization, but it must be borne in mind that *undissociated water is always formed*, whereas undissociated salt is usually *not* formed unless the water is first driven off.

SUMMARY

Metallic Conductance: All metals conduct electricity without suffering perceptible changes.

Non-Conductors: Dry non-metallic substances, including compounds of metals, do not conduct electricity.

Electrolytic Conductance: Pure water is a non-conductor of electricity. Dry acids, bases, and salts also are non-conductors. But water solutions of acids, bases, and salts conduct. Electrolytic conduction, however, is different from metallic conduction in that solutions of acids, bases, and salts undergo chemical change during the passage of an electric current.

The ionic theory assumes that when an acid, base, or salt is dissolved in water, its molecules become separated into two components called *ions*. Furthermore, the ions are heavily charged with positive and negative electricity, respectively.

Attraction and Repulsion: Bodies bearing like electric charges repel each other, whereas bodies with unlike charges attract.

Thus positively charged ions in solution attract and hold an electrically equivalent number of negatively charged ions. The ions are free to move past each other and they are all the time exchanging partners, but it is not possible for ions of one kind to exist in solution except when balanced by ions of opposite charge in their immediate vicinity.

Ions convey the electric current which passes through a solution.

Hydrogen ions are responsible for the properties of acids.

Hydroxyl ions are responsible for the properties of bases.

Salts, strong acids, and strong bases conduct strongly and are highly ionized when dissolved in water.

Weak acids and weak bases contain proportionately fewer ions than strong acids and bases. Thus the conductance for electricity and the acid and basic properties are weaker.

Substances enter readily into reaction when in the ionized condition, because their components are separated and thus free to exchange partners. When un-ionized, the components are rigidly bound together and substances do not readily enter into reaction.

Neutralization according to the ionic theory consists in the pairing of positive hydrogen ions of the acid with negative hydroxyl ions of the base to form undissociated water. The negative radical ions of the acid and the positive metal ions of the base remain in the solution as a dissociated salt. The undissociated dry salt is obtained by evaporating off the water.

Questions

1. In what important respect is acid hydrogen different from ordinary hydrogen? To what is this difference attributed?

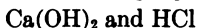
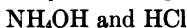
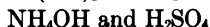
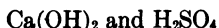
2. What component of all bases causes litmus to become blue? of all acids causes litmus to become red?

3. Why do solutions of acids, bases, and salts conduct the electric current, whereas the dry substances are non-conductors?

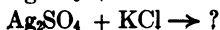
4. Explain in terms of the ionic theory why carbonic acid is so much weaker than sulphuric acid.

5. What argument can you advance in favor of the truth of the ionic theory, other than those drawn from the conductivity of solutions of electrolytes?

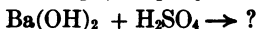
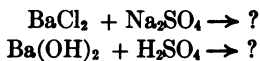
6. Formulate in terms of the ionic theory what takes place during the neutralization of



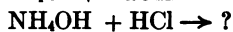
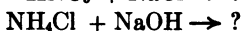
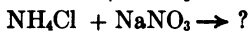
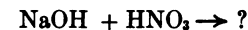
7. Remembering that silver chloride is insoluble, write ionized equations for the following cases



8. Remembering that barium sulphate is insoluble, write ionized equations for the following cases



9. Remembering that all sodium, potassium, and ammonium salts are soluble, write ionized equations for the following cases



CHAPTER XXVI

ELECTROLYSIS

328. Electrolysis of Hydrochloric Acid. When a solution of hydrochloric acid is electrolyzed, hydrogen gas is given off at the negative pole and chlorine gas at the positive pole (Chapter XIII). The poles, or electrodes, should consist of strips of platinum, because platinum is attacked but little by either the acid or the chlorine. The electrodes are immersed at opposite sides of the solution and they are connected by metal wires with the electric cell or the dynamo (Fig. 61).

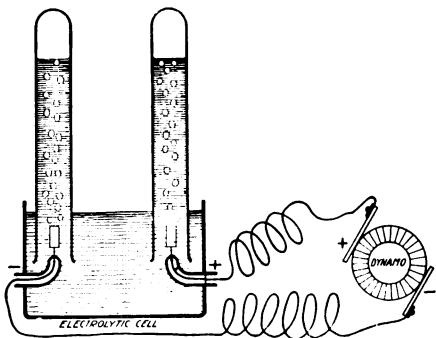
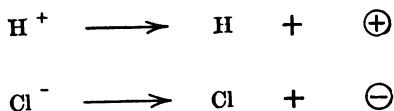


FIG. 61. — Electrolysis of Hydrochloric Acid.

Thus one electrode is kept constantly charged with positive electricity and the other with negative electricity. Since chlorine is given off at the positive pole, the chlorine must first have been attracted through the solution to the surface of the pole, and since it is attracted to a positively charged body, it must itself be negatively charged. By the same reasoning, since hydrogen is given off at the negative electrode, the hydrogen in the solution must be positively charged.

329. Discharge of Ions. It is, of course, obvious that ordinary hydrogen gas and chlorine gas are not electrically charged. Before their escape from the surface of the electrodes, the hydrogen and chlorine ions, respectively, must have surrendered their electric charges,



The electric charges thus given up to the electrodes neutralize the opposite charges which are being continually supplied from the dynamo.

330. Ions as Carriers. The ions which come up to the electrodes during the electrolysis and give up their charges are bringing a steady supply, or current, of electricity. They may be likened to a line of laborers each with a wheelbarrow load of gravel. Each laborer comes up in turn, discharges his load of gravel in the desired place, and steps aside with his wheelbarrow. In the same way a file of H^+ ions moves towards the negative electrode. As each ion reaches the electrode, it discharges its load of electricity and retires to form hydrogen gas (by doubling up with the next hydrogen atom released). A file of Cl^- ions moves at the same time in the opposite direction, and each ion in turn gives up its charge at the positive electrode and retires to form ordinary chlorine gas (by pairing with the next atom of chlorine).

Let us picture the process by means of diagrams. Let a white circle $\bigcirc$ represent a hydrogen atom and a circle with a + sign $\bigoplus$ represent a hydrogen ion. Let a black circle $\bullet$ represent a chlorine atom and $\ominus$ a chlorine ion. At the outset let us represent six of each kind of ions in the solution be-

tween the electrodes instead of the countless number which is actually present (Fig. 62). After the current has passed for some time, a certain number of ions — let us say two of each kind — has been discharged. The two H^+ ions nearest the negative electrode have moved up to it and discharged.

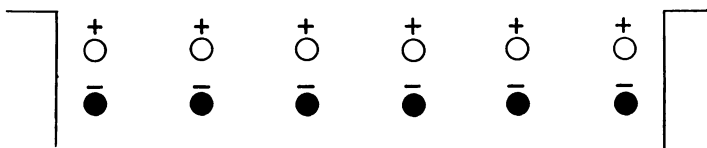


FIG. 62. — Ions in Solution before Current has passed between Electrodes.

This leaves unbalanced the two Cl^- ions which were originally paired with the two H^+ ions. It is impossible for them to remain long unbalanced. They are repelled by the negatively charged electrode and they move away from it, but in moving away they repel the four Cl^- ions in front of them. At the same time they attract the hydrogen ions farther down the line and these move up to balance them. At the other electrode a similar process has taken place; two chlorine ions have discharged and left two hydrogen ions unbalanced. The latter are repelled and move away, following the other hydrogen ions. At this point in the electrolysis we have

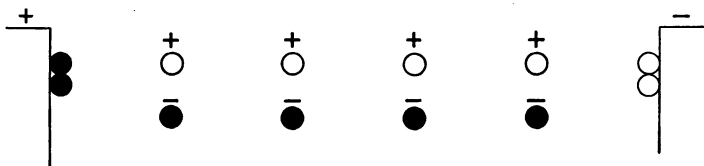


FIG. 63. — Showing Condition of Solution from Fig. 62, after Current has passed for a Time.

positive and negative ions balanced against each other throughout the solution just as at the outset, but there are only four pairs now instead of six as at first (Fig. 63);

and accumulated on the poles we have a molecule of hydrogen and a molecule of chlorine, respectively.

If the electrolysis were continued long enough, all the ions would be withdrawn from the solution and nothing but pure water would be left. In such a case, of course, the current would stop flowing, for there would be nothing left to conduct it; for pure water is a non-conductor.

331. Atomic Structure of Electricity; Electrons. It has probably occurred to the reader to wonder what determines just how much electricity each ion carries. Evidently the positive charge of the hydrogen ion is just equal and opposite to the negative charge of the chlorine ion; and it is almost equally evident that every hydrogen ion always has just the same amount of positive electricity and every chlorine ion has just the same amount of negative electricity. One might well wonder if electricity does not have an *atomic* structure just like ordinary matter and if the charge on the hydrogen ion is not really a single atom of positive electricity and the charge on the chlorine ion a single atom of negative electricity. That this is really so seems extremely probable in the light of our present knowledge, and we shall from now on speak of the electric atoms as confidently as we speak of the atoms of the material elements. We shall call these smallest divisions of electricity *electrons* and we shall distinguish positive and negative electrons and give them the symbols $\oplus$ and $\ominus$.

Recent study of electric discharges in vacuum tubes, and work with the wonderful element radium have thrown a great deal of light on the subject of electrons. The negative electrons have actually been discovered unassociated with ordinary matter, in the discharge from the negative electrode in vacuum tubes. Positive electrons have never been found except in association with atoms of the ordinary elements.

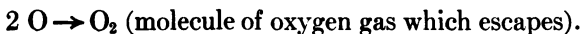
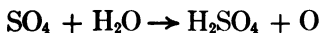
It may be that only what we call the negative electrons have a real existence and that what we call positive electrons are merely atoms of ordinary matter deprived of negative electrons which belong there. We shall find it convenient to speak of both positive and negative electrons as well as of positive and negative electricity as if both existed, and we shall not concern ourselves with the question as to whether there are really two kinds or only one kind of electricity.

332. Electrolysis of Sulphuric Acid. Sulphuric acid contains hydrogen and a sulphate radical. Since the acid gives H^+ ions when it dissociates, the sulphate radical must form the negative ions :



When this acid is electrolyzed, it might be expected that SO_4^{--} ions would travel towards the positive electrode and H^+ ions towards the negative electrode. As a matter of fact, hydrogen is given off at the negative electrode, but at the other electrode oxygen is set free instead of the SO_4 radical.

The electrolysis of most substances is a more complicated phenomenon than that of hydrochloric acid, in which the ions that carry the current simply discharge and the respective elements escape in the uncombined condition. The SO_4^{--} ion of sulphuric acid is actually the carrier of the negative electricity, but the uncharged SO_4 radical is incapable of existence alone. When it parts with its electricity it would either itself have to break down into other substances or it would react with the solvent water. The latter is probably what happens and it is thus the oxygen of the water that escapes.



The sulphuric acid thus formed in this *secondary reaction* of course dissociates immediately into ions under the influence of the water.



333. It will be remembered that in decomposing water by the electric current (page 103), sulphuric acid was added in order to make the solution conduct. It was then stated that the sulphuric acid suffered no change but that only the water was decomposed, and it is now seen why the statement was justified. It is really the ions of sulphuric acid that carry

the current, but for every molecule of sulphuric acid that is drawn apart another molecule is generated by the secondary reaction at the positive electrode, and the amount of sulphuric acid in the whole solution suffers no change.

334. If what has just been said is true, there must, however, be an accumulation of sulphuric acid around the positive electrode and a depletion around the negative electrode, for the SO_4^{--} ions are drawn away from the latter and the H^+ ions are discharged there. We ought to be able to show this accumulation and depletion in order to justify our arguments.

In the apparatus shown in Fig. 61

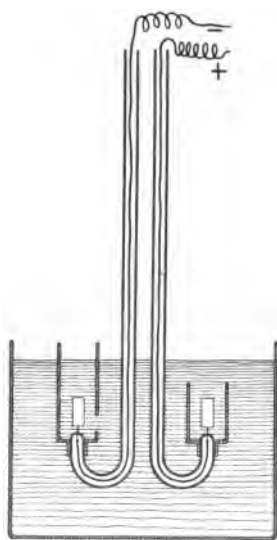


FIG. 64. — **Electrolysis of Sulphuric Acid.** Arranged to prove the passage of sulphate ions away from the - electrode and towards the + electrode.

would be continually in circulation and on this account no accumulation of sulphuric acid would last long enough

to be demonstrated. It is necessary to modify the apparatus somewhat and to arrange glass cups around the electrodes to prevent circulation of the liquid (Fig. 64). Where the sulphuric acid accumulates, the cup must be open at the top and closed at the bottom because the more concentrated a solution the heavier it is. Where the sulphuric acid is depleted, the cup must have an opening at the bottom for the passage of the current and the top must rise above the surface of the liquid because the acid of diminished concentration is lighter than the original acid.

If after the current has passed for some time through a dilute solution of sulphuric acid in this apparatus, portions of the solution are removed with a pipette (Fig. 65) from the two

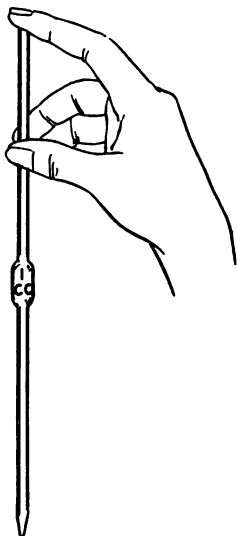


FIG. 65. — Pipette.

cups and analyzed, it is actually found that the one from the cup around the negative electrode contains less sulphuric acid and that from the cup around the positive electrode more sulphuric acid than at the start.

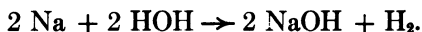
335. Secondary Reaction at Electrodes. As already stated, it is not always true that the products which appear at the electrodes as a result of electrolysis are formed directly from the ions that carry the current through the solution. These products arise quite as often from *secondary reactions* which the discharged ions enter into either among themselves or with water. It is hence not possible to say from an observation of the products liberated at the poles what are the ions in the solution. In the electrolysis of sodium hydroxide

and sodium sulphate, for example, the products liberated are hydrogen and oxygen. These gases are evolved in the proportion of two volumes of the former to one of the latter, just as in the electrolysis of dilute sulphuric acid. We have thus a typical acid, a typical base, and a typical salt all of which yield as the final products of their electrolysis only the two constituents of pure water. Yet these substances cannot all have the same ions.

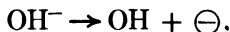
336. Electrolysis of Sodium Hydroxide. It has already been stated that the ions of sodium hydroxide are Na^+ and OH^- and it must be these that carry the current. At the negative electrode we may imagine the Na^+ ion to be discharged,



and the sodium atom to react with water,



At the positive electrode, we may imagine that the OH^- ions discharge,



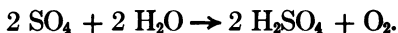
and that the hydroxyl groups so formed react together to give water and oxygen gas:



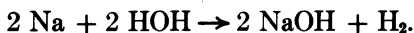
We have taken for granted that hydrogen is only the secondary product of the electrolysis and that it results from the reaction of the water on the sodium which is first set free. If it were possible to electrolyze sodium hydroxide without using water as a solvent, it might be possible to obtain metallic sodium instead of hydrogen at the negative electrode. Dry, solid sodium hydroxide does not conduct electricity; but if heated strongly it melts, and the liquid sodium hydroxide is an excellent electrolytic conductor. Metallic sodium

is then obtained as a deposit at the negative electrode, and this is one of the methods by which metallic sodium is manufactured on a commercial scale.

337. Electrolysis of Sodium Sulphate. Sodium sulphate is the salt obtained by neutralizing sodium hydroxide with sulphuric acid, and its solution contains the same metal ion as the base and the same radical ion as the acid. Thus on electrolyzing a sodium sulphate solution, since the negative ion is the same, the same change occurs at the positive pole as when sulphuric acid is electrolyzed, namely, the ion discharges and the sulphate radical reacts with water,



At the negative electrode the same change occurs as when sodium hydroxide is electrolyzed, namely, the sodium ion discharges and the metal atom then reacts with water,



Sodium sulphate is a neutral salt and its solution does not change the color of either red or blue litmus. If the solution is electrolyzed, however, in an apparatus similar to that shown in Fig. 64, in which both electrodes are surrounded by cups, a piece of litmus placed in the cup around the positive pole will immediately turn red, showing that an acid is formed, and the piece of litmus in the other cup will immediately turn blue, showing that a base is produced. By glancing back to the equations for the secondary reactions, one sees that in accounting for the formation of the hydrogen and oxygen, it was necessary to allow also for the formation of sodium hydroxide and sulphuric acid at the respective electrodes. The formation of base and acid at the two poles agrees, therefore, with our interpretation of the secondary reactions and increases our confidence in the correctness of our deductions.

If the reactions are studied a little further, it will be seen that since two atoms of hydrogen are liberated for each atom of oxygen, two molecules of sodium hydroxide should be formed at the one pole for each molecule of sulphuric acid at the other. These are equivalent quantities, and should just neutralize each other. Now if to test this deduction the whole solution is thoroughly mixed after the electrolysis has been stopped, it is found that the solution becomes again perfectly neutral and will not change either red or blue litmus. Thus there are in fact exactly equivalent quantities of acid and base produced by the electrolysis of the salt.

338. Electrolysis of Sodium Chloride. One of the important commercial methods of manufacturing sodium hydroxide is by the electrolysis of sodium chloride, the most abundant and least expensive compound of sodium. The sodium hydroxide is obtained at the negative electrode, and chlorine, which is an even more valuable product, is obtained at the other electrode (see Chlorine, Chapter XVI).

Sodium is one of the most active of all metals and it is because of this that sodium does not appear as one of the products when solutions of sodium salts are electrolyzed. No more do we obtain potassium or calcium when solutions of their salts are electrolyzed; we obtain, instead, the bases potassium hydroxide and calcium hydroxide, just as we obtained sodium hydroxide by the electrolysis of a sodium salt.

339. Electrolysis of Copper Sulphate. When, however, a salt of a metal which does not decompose water is electrolyzed, the metal itself ought to be obtained. For example, if the current is passed through a solution of copper sulphate, CuSO_4 , between platinum electrodes, a reddish metallic deposit of copper begins at once to appear on the negative pole.

while at the other pole oxygen escapes. The copper ions simply surrender their charges to the electrode,



and the unelectrified atoms stick there and soon build up a coherent layer of the metal. At the other electrode, the ions which come up to discharge are the same as with sulphuric acid or sodium sulphate, and so long as the electrodes are of the unattackable metal platinum, the reaction is the same as already described under the electrolysis of these substances.

340. The electroplating of copper is an art of very great importance. The object to be covered is made the negative electrode in a bath of a copper salt, frequently copper sulphate; for the other electrode a thick plate of copper is used instead of platinum or other unattackable metal. Now, when the current passes, Cu^{++} ions discharge at one electrode and this would, after a while, deplete the bath of copper except that the metal of the other electrode dissolves and maintains the supply. The SO_4^{--} ions are attracted to the positive electrode as usual, but instead of having to give up their charges, they become electrically balanced by new copper ions which are formed from the metal of the electrode and the positive electricity.



Thus electroplating consists merely in transferring copper in the form of ions through a solution from a thick mass of the metal to the object to be plated. (Compare Electrolytic Refining of Copper, page 254.)

341. Multiple Proportions among Ionic Charges. Of the several ions mentioned in this and the preceding chapter, it is noticed that some are represented as carrying single charges of electricity, or single electrons, whereas others are repre-

sented as having exactly twice as much electricity, that is, two electrons each. Following is a table giving some of the very common ions and showing the number and character of the charges on each :

Hydrogen	H ⁺	Chloride	Cl ⁻
Sodium	Na ⁺	Nitrate	NO ₃ ⁻
Potassium	K ⁺	Bromide	Br ⁻
Ammonium	NH ₄ ⁺		
Silver	Ag ⁺		
Calcium	Ca ⁺⁺	Sulphate	SO ₄ ⁻⁻
Copper	Cu ⁺⁺	Carbonate	CO ₃ ⁻⁻
Barium	Ba ⁺⁺		
Zinc	Zn ⁺⁺		
Magnesium	Mg ⁺⁺		
Aluminium	Al ⁺⁺⁺	Phosphate	PO ₄ ⁻⁻⁻

The fact that the amount of electricity on an ion is always some whole multiple of the unit amount that resides on the H⁺ ion or the Cl⁻ ion was originally the reason for wanting to ascribe an atomic structure to electricity. If electricity were continuous in nature and not atomic, it would be hard to see why some ions should bear exactly the unit charge, some exactly twice, and some exactly three times the unit charge, but none should ever bear fractional amounts. As already stated, page 314, the idea of the atomic, or electronic, structure of electricity is now firmly established.

342. Faraday's Law. It was observed as long ago as early in the nineteenth century that when chemical decompositions were caused by the passage of the current, there was a simple relation between the amounts of different substances decomposed by the same quantity of electricity. The relation was first clearly recognized by Faraday, and the law which expresses this relation is known as Faraday's law.

We may state the law as follows: *The passage of the same amount of electricity causes the liberation of equivalent amounts of different substances at the electrodes.* We have already seen that two volumes of hydrogen are liberated at one electrode while one volume of oxygen is set free at the other. These are equivalent quantities, for they are the amounts which combine with each other to form water. We have also seen that equivalent amounts of acid and base are formed at the electrodes when a salt solution is electrolyzed.

343. When an electric current flows in a given circuit, it is true that the quantity which passes in any one part of the circuit is exactly the same as that which passes any other part of the circuit. Let us construct a circuit with several electrolytic cells as shown in Fig. 66, the first cell having silver electrodes in silver nitrate solution, the second copper electrodes in copper sulphate solution, the third platinum electrodes in sulphuric acid, and the fourth platinum electrodes in sodium sulphate solution.

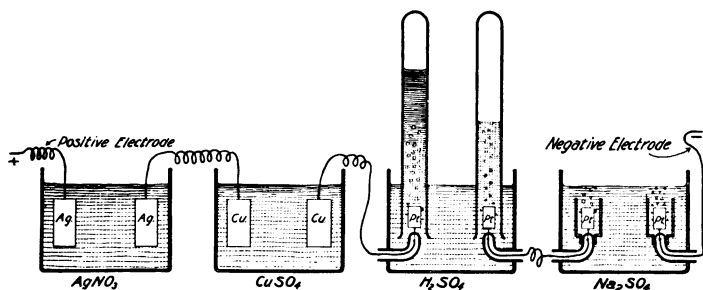


FIG. 66. — Electrolytic Cells in Series.

Let us now allow an amount of electricity to pass which is sufficient to carry 108 grams of silver from the positive electrode into the solution and to deposit 108 grams of silver on the negative pole of the first cell, and let us observe what

corresponding changes take place in other parts of the circuit. 108 is the atomic weight number of silver and 108 grams is the gram-atomic weight.

In the second cell, we find that 31.8 grams of copper are dissolved from the positive electrode and that an equal amount is deposited on the negative electrode. The atomic weight of copper is 63.6; hence 31.8 grams is one half an atomic weight in grams. This amount of copper, then, is equivalent to 108 grams or a whole atomic weight in grams of silver, electrically as well as chemically. Chemically, an atom of copper is equivalent to two atoms of silver, for it has twice the capacity for holding atoms of non-metallic elements in combination. This is shown, for example, by comparison of the oxides and chlorides:



In the third cell of the series, 5.6 liters of oxygen gas (measured under standard conditions) are liberated at the positive electrode and 11.2 liters of hydrogen gas at the negative electrode. These quantities are equivalent to the amounts of silver and copper deposited in the first two cells, for a simple calculation will show that 11.2 liters of hydrogen weigh 1 gram and thus equal one gram-atomic weight of that element, and that 5.6 liters of oxygen weigh 8 grams and thus equal one half gram-atomic weight of the latter element.

In the fourth cell of the series, a chemical analysis of the solution in the cup around the negative electrode would show that 40 grams or one mole of sodium hydroxide is produced, and an analysis of the solution at the other electrode would show that 49 grams or one half mole of sulphuric acid is produced. These amounts are equivalent to each other

and to the amounts of silver, copper, hydrogen, and oxygen involved in the other cells.

344. The foregoing illustrations have shown the wide application of Faraday's law. Every year the application of electricity in chemical manufactures is growing more and more extensive. From a knowledge of Faraday's law and the electrochemical equivalent, it is possible to figure just how much electric current will be required to carry out any desired electrochemical process, and the practical electrochemist makes constant use of this law in his calculations.

SUMMARY

Electrolytic conduction is always accompanied by a chemical decomposition. In the simplest case of electrolysis, the ions of the dissolved substance discharge and the two constituents appear at the electrodes. Thus the electrolysis of hydrochloric acid gives hydrogen and chlorine, respectively.

Secondary Reactions: In many cases, the discharged ions yield chemically active elements or radicals which enter into a secondary reaction with the solution so that the products actually liberated do not correspond with the ions that take part in the conduction through the liquid.

Electroplating: In the electrolysis of the salts of the less active metals, the metals themselves are deposited, or plated, on the negative electrode. In this wise the extensive art of electroplating is carried out. To avoid depletion of the metal in the solution, the positive electrode is made of a heavy mass of the metal to be plated, and the metal then dissolves from this electrode as fast as it is deposited upon the other.

Faraday's Law: The passage of the same amount of electricity causes the liberation of chemically equivalent amounts of different substances at the electrodes. The electricity required to set free one gram-atomic weight of any element whose ions carry a single electron, will set free one half gram-atomic weight of any element, or radical, whose ions carry two electrons.

Questions

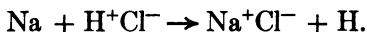
1. How does electrolytic conduction differ from that in a metallic conductor?
2. What becomes of the charges which the ions carry up to the electrodes?
3. What would happen if a dilute solution of H_2SO_4 were to be electrolyzed for a long time?
4. What becomes of the sulphate radical when H_2SO_4 is electrolyzed?
5. What becomes of the metallic sodium which one might expect to get at the negative electrode when sodium hydroxide solution is electrolyzed?
6. What facts prove that there is a greater concentration of sulphate ions around the positive electrode than anywhere else in the solution during the electrolysis of H_2SO_4 ?
7. How does it happen that the acid formed around the positive electrode during the electrolysis of sodium sulphate solution exactly neutralizes the base formed around the negative electrode?
8. What sort of metals would be obtained in the metallic state on the negative electrode during the electrolysis of their salts?
9. Show how practical use is made of the above type of electrolysis.
10. Try to devise a means of measuring electricity based upon what you have just learned about Faraday's law.
11. What weight of silver would be deposited from AgNO_3 solution by the same current that deposits 6.36 grams of copper from $\text{Cu}(\text{NO}_3)_2$ solution?
12. A certain amount of electric current liberates 27.1 kilograms of aluminium from the solution of aluminium oxide in fused cryolite (page 260). How much copper would the same current deposit on the negative electrode in copper refining (page 254)?

CHAPTER XXVII

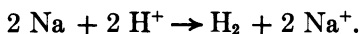
THE ELECTROMOTIVE SERIES

345. Displacement of Hydrogen by Metals. It has already been seen in the chapters on the Ionic Theory and on Electrolysis that the peculiar properties of acid hydrogen are in all probability due to the latter being in an ionized condition and carrying positive electric charges.

When an active metal, such as aluminium, magnesium, or sodium, reacts with an acid and sets free hydrogen gas, a salt of the metal is formed in the solution and we know that this salt is ionized; we also know that the hydrogen as gas is no longer ionized, for it is not possessed of any free electric charge. The metal must then have taken the electric charges away from the hydrogen ions, and the hydrogen atoms without the charges have combined to form the molecules, H_2 , of ordinary hydrogen. Thus the displacement of hydrogen by metallic sodium may be represented as follows:



In order to obtain molecular hydrogen, this equation must be taken twice so as to give two atoms. Since the chlorine ion remains unchanged, it may be omitted from both sides in writing the equation and thus we have



The metal on acquiring the positive charges from the hydrogen passes into the form of ions and as such no longer exists

as a compact metallic mass, but forms a component of the solution, whereas the hydrogen on passing out of the ionic condition ceases to be a component of the solution.

346. Displacement of One Metal by Another. Not only can an active metal displace hydrogen from the solution of an acid, but it can displace metals less active than itself from the solutions of their salts. For example, when a knife blade is dipped into a solution of copper sulphate, a copper-colored coating is at once deposited on the blade. The coating is copper, and at the same time that it is being thrown down, iron from the knife blade is passing into solution. It is true that the passage of iron into the solution cannot be seen as can the depositing of the metallic copper, but we can easily convince ourselves that it takes place; for if after a little while the solution is tested chemically, it is found to contain iron ions. Iron displaces hydrogen from sulphuric acid and in just the same way that it displaces the copper from copper sulphate, except that free un-ionized copper forms a compact metallic mass rather than a gas. The atoms of iron of course acquire electric charges and pass into the solution as ions, while simultaneously the copper ions lose their charges and are deposited as metallic copper:



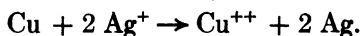
or, since the sulphate ion is unchanged,



A number of active metals besides iron can displace copper and hydrogen from solutions. Among them are the extremely active metals sodium and potassium, which react with great violence, the active metals magnesium, aluminium, and zinc, which react rapidly, and the moderately active metals such as tin and lead, which react rather slowly. Not

only do these metals displace hydrogen and copper, but they displace the precious metals, silver, gold, and platinum, from solutions of their salts. In fact, copper itself displaces the metals silver, gold, and platinum.

If a little piece of clean copper is placed in some silver nitrate solution in a test tube, a moss-like deposit begins at once to form over the surface of the metal. The deposit is metallic silver, and it appears mossy because it is built up of tiny branching crystals instead of forming a smooth uniform layer. At the same time the solution acquires a blue color which is due to the blue copper ions that are formed.



Copper ions always possess the same blue color whatever the negative ions that balance them. Thus dilute solutions of copper nitrate, copper sulphate, and copper chloride all possess exactly the same color.

347. Electromotive Series. All metals seem to possess a tendency to pass into the form of ions when in contact with water or with a solution. The magnitude of this tendency is enormous with metals like sodium and potassium; it is less, although large, with magnesium, aluminium, and zinc; it is small with iron, tin, and lead; and, finally, it is very small with the precious metals. The metals can all be arranged, as in the table, in the order in which they possess this tendency, and the series so obtained is known as the *electromotive series*.

348. Hydrogen is given a position in this series because it is like the metals in that it

Potassium
Sodium
Calcium
Magnesium
Aluminium
Zinc
Iron
Nickel
Tin
Lead
Hydrogen
Copper
Mercury
Silver
Platinum
Gold

Electromotive
Series.

forms simple, positive ions. Any metal in this series can drive any metal standing below it from the ionic into the metallic condition, whereas its own ions can be driven out of solution by any metal standing above it. Thus all the metals standing above hydrogen cause the evolution of hydrogen gas, when placed in an acid solution, but the metals copper, silver, mercury, gold, and platinum, which stand below, do not displace hydrogen.

349. Sodium reacts violently even with pure water and liberates hydrogen. Water itself ionizes to an infinitesimal extent, although so little that this point has been ignored in all our previous discussions. Sodium is so very active that it reacts even with the few hydrogen ions in water and drives them out. This quantity would be altogether too small to be perceptible, except that, with these ions removed, the water dissociates further so as to keep up its normal infinitesimal supply of ions. The sodium continues to react with these few ions, and new ones are continually formed in their place, so that in the end the sodium has all reacted and liberated an equivalent amount of hydrogen from the water which at the outset was practically un-ionized.

350. The farther above hydrogen a metal stands in the electromotive series, the greater is its tendency to pass into the form of ions, and consequently the more rapidly should it be able to displace hydrogen. By testing all of the metals with an acid, for example dilute hydrochloric acid, one finds that the metals towards the top of the list cause a violent evolution of hydrogen; that those lower down react less vigorously; that tin and lead, which stand only just above hydrogen, displace hydrogen, but so slowly that it might escape observation unless carefully looked for; and that all of the metals

below hydrogen in the list cause no evolution at all of hydrogen gas.

351. Electrochemical Equivalents. In the chapter on Electrolysis, it was found to be a law that the passage of the same amount of electricity causes the liberation of equivalent amounts of different substances at the electrodes. The law, which we know as Faraday's law, applies equally well to the displacement of one metal by another metal, and in reality the latter sort of displacement is just as much an electrolytic action as if the current entered by one electrode and left by another electrode. Here the same piece of metal serves as both electrodes in short electric circuits. At some points on the surface, its own atoms are passing into the solution as ions and taking positive charges with them, while at other points, the ions of hydrogen or other metal are depositing out of the solution and returning just as much positive electricity to the piece of metal as was given off at the first mentioned points. Hence the quantities of the different metals involved in these displacements are chemically equivalent quantities.

SUMMARY

Electromotive Series: All metals, in which classification hydrogen is included, have the ability, under proper conditions, to pass back and forth between the forms of ordinary massive metals, and positively electrified ions in solutions of the metal salts or of acids. The metals are arranged in a series in the order of their tendency to pass into the ionic form. This is known as the *Electromotive Series*.

Metals standing above hydrogen in the electromotive series set free hydrogen from acids; those standing below hydrogen cannot set hydrogen free.

As a general rule, a metal can drive any metal standing below it in the electromotive series from the ionic into the metallic

form. The amounts of the metals involved in such displacements are always equivalent.

Questions

1. Explain the difference between copper in the metallic condition and in solution — using the ionic theory in your explanation.

2. Write, in ionic form, the equation for the displacement of copper by iron. Assume that the copper was present as dissolved copper sulphate.

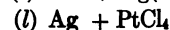
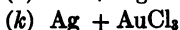
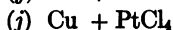
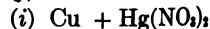
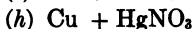
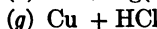
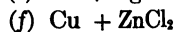
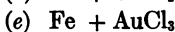
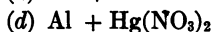
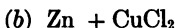
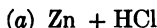
3. Between what two members of the electromotive series should we draw a line to separate those metals which *can* displace hydrogen from acid solution from those that *cannot*?

4. Why should hydrogen be included in a list of metals?

5. How is it possible that the active metals displace hydrogen from water?

6. According to Faraday's law — as applied to the displacement of one metal by another — what weight of metallic copper would be displaced by 56 grams of iron? By 65 grams of zinc? By 24 grams of magnesium? By 27 grams of aluminium? b34M

7. Write in ionic form equations for the following :



CHAPTER XXVIII

HYDROGEN EQUIVALENTS AND VALENCE

352. It is of the utmost importance in chemistry to know what amounts of different elements can mutually displace each other or combine with one another. If these amounts are always referred to the same standard, they are known as *equivalent weights*, and for the standard of reference, one gram atomic weight, that is practically one gram of hydrogen, is used.

The hydrogen equivalent of any metal is that weight of the metal which is required to displace one gram of hydrogen, or, in the case of a metal standing below hydrogen in the electromotive series, it is that weight of the metal which will be deposited by the same quantity of electricity as will set free one gram of hydrogen.

353. Experimental Determination of Hydrogen Equivalents. Let us consider in some detail the actual steps we would follow to determine the hydrogen equivalents of the three common metals, aluminium, magnesium, and sodium; and then let us study the results and see how they compare with the atomic weights of these metals.

To find the weight of aluminium which will displace one gram of hydrogen from an acid, we take a little piece of pure aluminium wire and weigh it accurately. It weighs 0.0388 gram in a specific case that we are considering. The wire is placed in the bottom of a good-sized beaker and over it is placed an inverted funnel to direct the hydrogen gas

into the collecting vessel (Fig. 67). The beaker is now filled with water until the stem of the funnel is covered. To measure the hydrogen gas, we take a 100 c.c. measuring

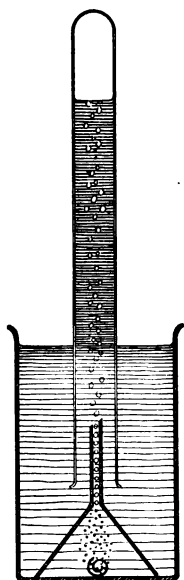


FIG. 67. — Determining the Hydrogen Equivalent of a Metal.

tube such as that used for determining the volume per cent of oxygen in air (page 74). This tube is filled completely with hydrochloric acid, the thumb is placed over the mouth of the tube, and the latter is then inverted over the stem of the funnel in the beaker. When the thumb is removed, the heavier acid sinks through the water to the bottom of the beaker where it comes in contact with the aluminium and reacts with it. The hydrogen evolved rises through the stem of the funnel and into the measuring tube. When all the aluminium has reacted, the tube is somewhat more than one half filled with hydrogen, the volume of which is now to be accurately measured. The thumb is again placed over the mouth of the tube, and without allowing any gas to escape or

air to enter, the tube is transferred to a deep vessel of water where its height is so adjusted that the water level inside the tube is the same as that outside. The volume is then read off from the markings on the tube and at the same time the temperature and the barometric pressure are noted. The data thus obtained are :

Weight of aluminium	0.0384 g.
Measured volume of hydrogen	53.4 c.c.
Temperature	20° C.
Barometric pressure	740 mm.

We know that one liter of hydrogen under standard conditions weighs 0.09 gram, but before we can calculate the weight of the gas obtained, we must find its volume under standard conditions.

Applying the correction for temperature:

$$53.4 \text{ c.c. at } 20^{\circ} = 53.4 \times \frac{273}{293} = 49.8 \text{ c.c. at } 0^{\circ}$$

and for pressure:

$$49.8 \text{ c.c. at } 740 \text{ mm.} = 49.8 \times \frac{740}{760} = 48.5 \text{ c.c. at } 760 \text{ mm.}^1$$

This volume weighs:

$$\frac{48.5}{1000} \times 0.09 = 0.00427 \text{ gram.}$$

We have now found that 0.0384 gram of aluminium displaces 0.00427 gram of hydrogen. Therefore x grams of aluminium will displace 1 gram of hydrogen.

$$\frac{0.0384}{x} = \frac{0.00427}{1}$$

$$x = \frac{0.0384}{0.00427} = 9.0 \text{ grams Al}$$

and the hydrogen equivalent of aluminium is 9.

Experiments carried out with magnesium and sodium² after the manner just described for aluminium show that 12 grams of magnesium are required to displace 1 gram of hydrogen and that 23 grams of sodium are required to displace 1 gram of hydrogen. The hydrogen equivalent of magnesium is therefore 12, and that of sodium is 23.

354. The atomic weights of these three elements are,

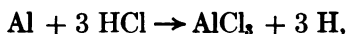
¹ This is only approximate, since water vapor is neglected.

² Sodium is so active that the method must be modified in some of its details.

aluminium 27, magnesium 24, and sodium 23. So it is seen that the hydrogen equivalent and the atomic weight are identical in the case of sodium; that the hydrogen equivalent of magnesium is one half the atomic weight; and that the hydrogen equivalent of aluminium is one third of the atomic weight. From this it follows that one atomic weight of sodium can displace a single atomic weight of hydrogen; that one atomic weight of magnesium can displace two atomic weights of hydrogen; and that one atomic weight of aluminium can displace three atomic weights of hydrogen.

355. Valence. *The number which expresses how many atomic weights of hydrogen are displaced by one atomic weight of an element is the valence of that element* (see section 215).

Thus, since one atomic weight of aluminium can take the place of three atomic weights of hydrogen when this metal reacts with an acid,



the valence of aluminium is three. Similarly the valence of magnesium is two, and that of sodium is one.

356. It has already been seen that hydrogen is more like the metals than the non-metals in its chemical properties. It forms positive ions like the metals, never negative ions as do the non-metals. It shows little ability to form compounds with the metals, to which it is similar in nature; but it does form compounds with the non-metals, to which it is dissimilar.

Hydrogen can take the place of, or be displaced by, metals, and the valence of a metal is measured by the amount of hydrogen to which it is equivalent. But the valence of a non-metallic element cannot be measured by the number of atomic weights of hydrogen that one atomic weight can

displace, because hydrogen and the non-metals, being opposite in their chemical nature, are not mutually interchangeable. But non-metals can *combine* with hydrogen, and their valence is measured by the number of atomic weights of hydrogen which one atomic weight of the element will hold in chemical combination.

The weight of chlorine which combines with 1 gram of hydrogen to form hydrogen chloride is 35.5 grams, and since this quantity is the gram-atomic weight of chlorine, it follows that chlorine combines with hydrogen, atomic weight for atomic weight, therefore the valence of chlorine is one.

The weight of oxygen which combines with 1 gram of hydrogen to form water is 8 grams. Since this is one half the gram-atomic weight of oxygen, it follows that one whole atomic weight of oxygen can combine with two atomic weights of hydrogen; therefore the valence of oxygen is two.

The weight of sulphur which combines with 1 gram of hydrogen is 16 grams. The atomic weight of sulphur is 32; hence 16 grams is one half of a gram-atomic weight. One whole atomic weight of sulphur combines with two atomic weights of hydrogen and the valence of sulphur is two.

357. When it is desired to know the valence of any element, it is only necessary to find the composition of its simple compounds. The knowledge of the composition of all the compounds that have been thoroughly studied is already at hand, and this knowledge is expressed in the chemical formulas of the compounds. Hence to find the valence of an element, we refer to the formulas of its simple compounds.

The formula of hydrogen chloride, HCl , tells us that chlo-

rine combines atomic weight for atomic weight, or atom for atom, with hydrogen and that the valence of chlorine is one. The formulas of water and hydrogen sulphide are H_2O and H_2S , respectively, and the valence of oxygen, as well as of sulphur, is therefore two.

358. In compounds containing no hydrogen, comparison must be made with the known valence of one of the elements of the compound. In the compound potassium chloride, whose formula is KCl , the valence of chlorine is known to be one, because chlorine has already been compared directly with hydrogen as stated above. Then since potassium combines with chlorine in the proportion of atom for atom, the valence of potassium must also be one. That this method of comparison is justified, may be shown from the hydrogen equivalent of potassium. It requires 39 grams of potassium, or one gram-atomic weight, to displace 1 gram of hydrogen.

The valence of magnesium is seen to be two by an inspection of the formula of magnesium chloride, MgCl_2 ; and the valence of aluminium to be three from the formula AlCl_3 .

359. Valence in Compounds Containing More than Two Elements. When three or more elements are present in a compound, the problem of finding the valence of each element becomes more complicated. More must be known about the mutual relations of the elements in the compound than is shown in the formula. Indeed, very different opinions are held to-day by the foremost chemists as to the real valence of some of the elements in complex compounds; and, such being the case, we shall not attempt here to go into the question. We shall satisfy ourselves with applying our ideas of valence to the compounds containing two elements only, and within these limits we shall find the conception of valence

to be of the greatest service in understanding chemical combinations.

360. Variable Valence. Many of the elements show different valences according to different conditions under which they combine with other elements. For example, sulphur may combine with either two or three atomic weights of oxygen per atomic weight of sulphur (see page 350). The valence of sulphur in sulphur dioxide, SO_2 , is four because the sulphur combines with two oxygens each of which has a valence of two against hydrogen. In sulphur trioxide, SO_3 , the valence of sulphur is six.

Many other cases of change of valence are known and in the table on page 340 is found a list of the commoner elements with their valences; in many instances it is seen that two or more valences are given opposite a single element.

361. The valence which an element shows toward hydrogen is very often different from the valence of the same element towards oxygen. Thus sulphur, which we have just seen has the valence of four or six towards oxygen, shows the valence of two against hydrogen in hydrogen sulphide, H_2S . A considerable degree of regularity in the valence of elements of different families as well as in the differences in the valences displayed towards hydrogen and oxygen, is shown in the periodic arrangement of the elements on the page facing the inside back cover.

362. As already hinted, the conception of valence and a knowledge of valence numbers is an invaluable aid in developing our knowledge of chemistry. For example, if we know the combining habits and the valence numbers of all the elements, we can predict with certainty how any two elements will combine in a compound of which we have no other knowledge.

TABLE OF THE COMMONER ELEMENTS, THEIR SYMBOLS, VALENCES, AND APPROXIMATE ATOMIC WEIGHTS

NAME	SYMBOL	ATOMIC WEIGHT	VALENCE	
			Towards Hydrogen or Metals	Towards Oxygen or Chlorine
Aluminium	Al	27	0	III
Antimony	Sb	120	III	III, V
Argon	A	40	0	0
Arsenic	As	75	III	III, V
Barium	Ba	137	—	II
Bismuth	Bi	208	0	III
Boron	B	11	—	III
Bromine	Br	80	I	I, III, V, VII
Cadmium	Cd	112	0	II
Calcium	Ca	40	—	II
Carbon	C	12	IV	IV
Chlorine	Cl	35.5	I	I, III, V, VII
Copper	Cu	63.6	—	I, II
Fluorine	F	19	I	0
Gold	Au	197	0	I, III
Helium	He	4	0	0
Hydrogen	H	1	—	I
Iodine	I	127	I	I, III, V, VII
Iron	Fe	56	0	II, III
Lead	Pb	207	0	II, IV
Lithium	Li	7	—	I
Magnesium	Mg	24.3	—	II
Manganese	Mn	55	0	II, III, IV, VI, VII
Mercury	Hg	200	0	I, II
Nickel	Ni	58.7	0	II, III
Nitrogen	N	14	III	III, V
Oxygen	O	16	II	—
Phosphorus	P	31	III	III, V
Platinum	Pt	195	0	II, IV
Potassium	K	39	—	I
Silicon	Si	28.3	IV	IV
Silver	Ag	108	0	I
Sodium	Na	23	—	I
Strontium	Sr	88	—	II
Sulphur	S	32	II	IV, VI
Tin	Sn	119	0	II, IV
Zinc	Zn	65.4	0	II

SUMMARY

The hydrogen equivalent is that weight of a metal that is interchangeable with 1 gram of hydrogen. This amount of the metal is equivalent both electrically and chemically to one gram-atomic weight of hydrogen.

The valence of a metal is the number of gram-atomic weights of hydrogen which are equivalent to one gram-atomic weight of the metal.

The valence of a non-metal is the number of gram-atomic weights of hydrogen which one gram-atomic weight of the non-metal holds in combination.

In compounds that contain no hydrogen, the valence of the elements is derived from comparison with compounds that do contain hydrogen.

The valence of an element in a simple compound is usually apparent from an inspection of the formula of the compound. The conception of valence is often difficult to apply to compounds that contain more than two elements.

Variable Valences: The same element frequently displays different valences under different conditions. The valence of an element towards hydrogen is often different from the valence towards oxygen.

The conception of valence is of great value in developing our knowledge of chemistry.

Questions

1. Define "hydrogen equivalent."
2. Explain how the weight of the hydrogen displaced by a known weight of a metal may be found without actually weighing the gas.
3. Calculate the hydrogen equivalent of cadmium from the following data: 0.112 g. of cadmium released 24.4 c.c. of hydrogen at 20° C. and 740 mm. (1 liter H_2 at standard conditions = .09 g.)
4. The atomic weight of cadmium is 112. Using the hydrogen equivalent calculated in Question 3, find the valence of cadmium.
5. Calculate what weight of zinc (atomic weight, 65 — hydrogen equivalent, 32.5) would be convenient to use in a hydrogen equivalent determination — the gas measuring tube having a volume of 100 c.c.

CHAPTER XXIX

SULPHUR

363. Familiar Forms and Uses of Sulphur. Sulphur is familiar to us in the uncombined state as a brittle, yellow, non-metallic substance. We can buy it at a drug store in the form of a yellow powder or of coarse lumps or sticks. Powdered sulphur is used as an ingredient of various salves on account of its germicidal properties and it is often given internally for the purpose of "purifying the blood." A familiar old-fashioned remedy for the blood, that very likely has a good deal of virtue, is a mixture of sulphur and molasses. Sulphur is boiled with lime and water to make "lime sulphur" spray for killing insect pests that destroy our fruit trees. Sticks of sulphur, or prepared sulphur candles, are burned in rooms after sickness in order to destroy lingering disease germs. Sulphur is likewise burned in clothes closets in order to kill moths. The suffocating fumes of burning sulphur, which are composed of sulphur dioxide, are familiar, and in view of their offensiveness, it is not surprising that they are powerful in destroying pests. Sulphur is used in large quantities to "vulcanize" rubber.

Sulphur under ordinary conditions is a crystalline solid. The masses which we more usually see are opaque because they are composed of a great number of very small crystals overlapping and interlacing. It is well known that if the clearest specimen of transparent glass is pulverized, the powdered mass thus obtained presents the opaque appear-

ance of snow. Thus with the mass of small sulphur crystals, each one of which by itself is transparent.

When sulphur crystallizes under the right conditions, that is, when the crystallization takes place very slowly, as for example in fissures

in the earth, clear transparent crystals of considerable size are formed. These crystals are very beautiful; they are bounded by smooth lustrous surfaces which lie in certain definite planes with reference to imaginary axes of the crystals. Some idea of their



FIG. 68. — Rhombic Sulphur Crystals, clinging to a fragment of rock broken from the interior of a cavity in the earth.

shape and appearance may be obtained from Fig. 68. It is easy to obtain very small crystals of this kind in the laboratory, and they are just as perfect in shape as the large ones. It is only necessary to dissolve some sulphur in carbon disulphide, a liquid in which it is very soluble, and to leave the solution in a watch glass for a little time while the carbon disulphide evaporates. A number of the small crystals are left in the watch glass when the liquid has gone. These crystals belong to a certain system of crystals known as the *rhombic* system, and they are therefore spoken of as rhombic sulphur crystals.

364. Allotropic Forms of Sulphur. It is well known that uncombined carbon can exist in different forms, as charcoal, graphite, and diamond (Chapter XXIII). Charcoal is

amorphous, that is, without definite shape, whereas the other two forms are crystalline as they occur in nature. Sulphur likewise is known in three different forms, although these forms do not differ so extremely from one another as do graphite and diamond. The rhombic crystals which have just been described are the most frequent of the three forms.



FIG. 69. — Monoclinic Sulphur Crystals.

Another crystalline variety of sulphur can be obtained if a mass of melted sulphur is allowed to cool and solidify slowly. These crystals appear in the shape of long needles, which belong to the so-

called monoclinic system, and are known as monoclinic sulphur. They can be obtained in the laboratory if sulphur is melted in a clay crucible and is then left undisturbed to cool. When a thin solid crust has just formed over the surface, if a hole is broken and the still liquid sulphur underneath is poured out, a loose mass of needle-like crystals is found to fill the interior of the crucible. An idea of their appearance can be obtained from Fig. 69.

Another form of sulphur, the so-called amorphous form, is obtained when melted sulphur, which has been heated to about 250°C ., is suddenly chilled as when it is poured into water. At first this cooled sulphur is of a consistency much like soft rubber, but on standing it gradually stiffens and becomes brittle like ordinary sulphur.

The common form of sulphur melts at 114.5°C . to a pale

yellow, mobile liquid. Liquid sulphur has one very surprising property, namely, when heated to a higher temperature, instead of growing even more mobile, as do liquid substances generally, it becomes viscous. At the same time it turns dark in color. At about 250°C . it is so viscous that the vessel containing it may be inverted without its running out. Above 250°C . it again grows less viscous and at 448°C . it boils and is converted into a pale yellowish-brown vapor.

365. Occurrence of Sulphur. Sulphur occurs in nature as uncombined sulphur; as sulphides of the heavy metals, especially of iron, copper, lead, and zinc; and as sulphates, calcium sulphate (gypsum is $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), barium sulphate, and lead sulphate.



FIG. 70.—A Block of Louisiana Sulphur. The molten sulphur is pumped from the wells into huge wooden bins. The solid block in the picture is 48 feet high. The boards have been removed from the front face of the bin but have been left at the end. The sulphur is broken from the front of the block with blasting powder and is loaded on to freight cars for shipment.

Uncombined sulphur is found in many parts of the earth, notably in Sicily, in volcanic regions where it is deposited from the volcanic gases in fissures in the rocks. It is also found in some places where its formation does not seem to be due to volcanic action, notably in Louisiana.

In Sicily sulphur is extracted from the rocks by melting, the heat usually being obtained by the crude method of burning a part of the sulphur itself. In Louisiana, where the deposits are deep beneath the surface, a novel method has been invented for extracting the sulphur. Pipes are driven to the sulphur-bearing stratum and superheated water is forced down. The sulphur is thus melted; it sinks to the bottom of the well and is pumped to the surface by means of compressed air and run into huge wooden bins, where it is allowed to solidify.

SULPHIDES AND HYDROGEN SULPHIDE

366. Sulphides. In its chemical properties, sulphur is in many respects like the typical non-metals, oxygen and chlorine, that we have already studied. It combines with metallic elements — including hydrogen — forming sulphides just as oxygen and chlorine form oxides or chlorides. For example, when iron or copper or zinc filings are mixed with powdered sulphur and heated in a test tube over a Bunsen burner, a reaction soon begins, and if the tube is then removed from the flame the reaction continues under the influence of the heat which it, itself, develops, and the incandescence spreads through every part of the mixture. The substance that remains is neither sulphur, nor the metal, but is the sulphide of the metal.

Sulphur also combines directly with hydrogen but not

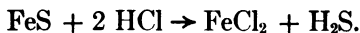
as energetically as with the metals. If sulphur is placed in a hard glass tube and a current of hydrogen is passed over the sulphur while the tube is heated with a Bunsen flame, a little hydrogen sulphide is formed, but the reaction is not energetic and continues to take place only so long as external heat is being supplied.

367. Hydrogen sulphide, H_2S , is a gas which has a very offensive odor, the odor of rotten eggs. It is frequently formed in the decomposition of organic matter containing sulphur, and thus its odor is apparent not only in eggs, but in sewage. When the mud of mud flats near where sewage is discharged is disturbed with a stick, the bubbles of gas which rise have a strong odor of hydrogen sulphide.

This gas is extremely poisonous to inhale. Breathing the undiluted gas will render a man unconscious almost instantly, and it will prove fatal unless he is immediately removed to the open air and restoratives are employed. Breathing very dilute hydrogen sulphide, as it is often present in the air of the laboratory, is offensive and may make one feel rather sick, but it is not especially dangerous.

The so-called sulphur water of sulphur springs is really water charged with hydrogen sulphide issuing from the interior of the earth. A small amount of hydrogen sulphide taken into the stomach in this way is not injurious and is in some cases perhaps even beneficial.

368. Laboratory Method of Preparing Hydrogen Sulphide. In the laboratory, hydrogen sulphide is made by allowing an acid to react with iron sulphide.



The desired product, being a gas, escapes as fast as it is formed and can be led as desired through delivery tubes.

369. Hydrogen Sulphide as a Precipitant. One of the most important uses of hydrogen sulphide is as a precipitant. If the gas is bubbled into the solution of a salt of copper, silver, mercury, lead, tin, or of any one of several other of the heavy metals, the sulphide of the metal is precipitated. Hydrogen sulphide is only slightly dissociated into ions, $\text{H}_2\text{S} \rightleftharpoons \text{H}^+ + \text{HS}^-$, but since the sulphides of the heavy metals are extremely insoluble, even the few sulphide ions from the hydrogen sulphide cannot remain in presence of the metal ions. Therefore metal sulphide precipitates, but as the sulphide ions are thus taken out of the solution, more hydrogen sulphide is able to dissociate and this continues until there are no more metal ions left to remove further sulphide ions.

By the formation or non-formation of a precipitate when hydrogen sulphide is passed into a solution, it is possible to tell whether salts of the heavy metals are present, and furthermore the color of the precipitate gives an indication as to what metal is present. Thus the sulphides of silver, lead, mercury, bismuth, and tin in the divalent condition precipitate from an acidified solution either black or very dark brown; the sulphides of cadmium, arsenic, and tin in the tetravalent condition, yellow; the sulphide of antimony, orange red. The sulphide of zinc precipitates white from a very weakly acid or an alkaline solution, but not from a strongly acid one; and from an ammoniacal but not from an acid solution, the sulphides of iron, nickel, and cobalt precipitate black and the sulphide of manganese, flesh-colored.

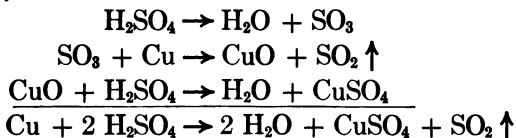
370. Hydrosulphuric Acid. A solution of hydrogen sulphide is faintly acid, — sufficiently so to barely turn blue litmus to red. This indicates a small content of hydrogen ions and corresponds to the low degree of dissociation re-

ferred to in the foregoing paragraph. If it is wished to lay emphasis on the fact that hydrogen sulphide is an acid, it is spoken of as hydrosulphuric acid (see page 221). It is almost never used for its acid properties, however, and hence we rarely see it mentioned by this name.

On the other hand, hydrogen chloride is a strong acid when it is dissolved in water, that is, its solution contains a large proportion of hydrogen ions. Its acid properties are the foremost in importance and we find it most commonly called hydrochloric acid.

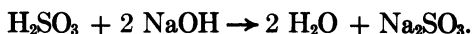
OXIDES OF SULPHUR

371. Sulphur Dioxide and Sulphurous Acid. It is well known that sulphur burns readily in the air and forms a very choking gas. This gas is sulphur dioxide, SO_2 . To prepare sulphur dioxide free from nitrogen and excess of air, the usual laboratory method is to heat together concentrated sulphuric acid and copper turnings. Sulphuric acid contains the oxide SO_3 in combination with water. The trioxide is reduced by copper to sulphur dioxide, which escapes as the gas desired. The copper is at the same time oxidized to copper oxide, and the copper oxide being a basic oxide reacts with surplus sulphuric acid to form the salt copper sulphate:

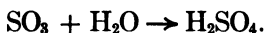


Sulphur dioxide is somewhat soluble in water and the solution is acid. It is supposed that a definite compound, sulphurous acid, is formed: $\text{H}_2\text{O} + \text{SO}_2 \rightarrow \text{H}_2\text{SO}_3$, but this

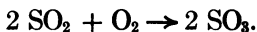
compound is so unstable that it is impossible to separate it out in the pure state from the water in which it is dissolved. The main reason for believing in the existence of this definite acid is that salts of the acid can be prepared. For example, the acid solution can be neutralized by adding sodium hydroxide; then, on evaporation of the neutral solution, a solid substance is left which on analysis is shown to have a composition corresponding to the formula Na_2SO_3 . This salt is sodium sulphite, and its relation to sulphurous acid is apparent from the mode of its formation:



372. Sulphur Trioxide and Sulphuric Acid. Although sulphur dioxide is the invariable product obtained when sulphur burns, it is not the only oxide of sulphur. Sulphur trioxide, SO_3 , is of still greater importance because of the fact that with water it gives sulphuric acid:



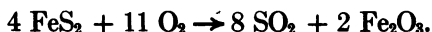
Sulphur trioxide is obtained by allowing sulphur dioxide to combine with more oxygen:



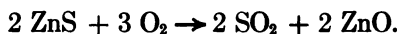
There is a good deal of chemical affinity between the sulphur dioxide and the oxygen and there is no difficulty in keeping them combined (as sulphur trioxide) if once they can be induced to unite. But the reaction by which they combine is sluggish, and very little sulphur trioxide can be obtained by merely bringing the two gases together, even if they are heated.

373. Manufacture of Sulphuric Acid. Since sulphuric acid is one of the most extensively used of chemicals, its

manufacture is of the greatest importance. There are two widely used processes for this. In both processes, the first step is the same, namely, burning sulphur to sulphur dioxide. Instead of free sulphur, iron pyrite, a sulphide of iron that is high in sulphur content, is often burned.



At zinc smelters, zinc sulphide ore must be roasted to convert it to zinc oxide:



Sulphuric acid plants are usually set up in such places so as to utilize the sulphur dioxide.

It is in the next step in the manufacture, namely, the conversion of sulphur dioxide to sulphur trioxide that the chief difficulty lies. The difficulty is overcome by the use of a *catalyzer*, which, as we have already seen, is a substance which does not undergo any permanent alteration itself, but by its mere presence causes an ordinarily sluggish reaction to become rapid. The difference between the two processes lies mainly in the different catalytic agents used.

374. Contact Process. In the so-called contact process, the catalytic substance is platinum. The action takes place at the surface of the metal; therefore, to present as large a surface as possible with a small quantity of this very expensive metal, the latter is spread out over asbestos fibers. The asbestos is dipped into a water solution of platinum chloride, it is dried and then ignited (heated strongly). The platinum chloride is decomposed and the metal is left in an extremely fine state of subdivision on the surface of the fibers. Tubes are now packed with this platinized asbestos,

and when these tubes are kept at a temperature of 400°C . and a mixture of sulphur dioxide and air is passed through them, the formation of sulphur trioxide takes place with great readiness.

To obtain sulphuric acid, it is only necessary to mix the sulphur trioxide with water (see equation on page 350). Although this would seem to be a very simple operation, it does, as a matter of fact, offer a good deal of difficulty, for the reaction produces great heat; and since sulphur trioxide is very volatile, a fearful smoke is produced if the mixing is not carried out with the greatest caution. In practice, the sulphur trioxide is not added directly to water but rather to a fairly concentrated sulphuric acid, as for example the acid that is obtained from the chamber process.

375. Chamber Process. In this process, oxides of nitrogen are used as the catalytic agent. There are a number of different oxides of nitrogen, among them being NO and NO_2 . Sulphur dioxide takes oxygen readily from the higher oxide, NO_2 , but the lower oxide NO thus formed takes oxygen at once from the air to form NO_2 again. The NO_2 again gives oxygen to sulphur dioxide and is immediately regenerated by taking on more oxygen from the air, and thus a very small amount of oxide of nitrogen by repeating the action a great many times can "carry" oxygen to a large amount of sulphur dioxide, whereas sulphur dioxide by itself is incapable of combining to any extent with the oxygen.

In practice, the sulphur dioxide from the sulphur or pyrite burners, together with an excess of air, is conveyed through a tower (see diagram, Fig. 71) which serves partly to cool the gases and partly to charge them with oxides of nitrogen. They are then allowed to pass through large lead chambers (sometimes as large as $100 \times 40 \times 20$ feet) where they be-

come thoroughly mixed and where the oxide of nitrogen gets a full opportunity to carry oxygen to the sulphur dioxide. To aid in this process as well as to furnish the water necessary to convert the sulphur trioxide into sulphuric acid, steam or water in a fine spray is blown into the lead chambers. The liquid sulphuric acid collects on the bottom of the chamber and from there is siphoned off.

From the last of the series of chambers, there is little left to pass out as gas except the nitrogen of the air used for the oxidations, and the oxides of nitrogen. These oxides of

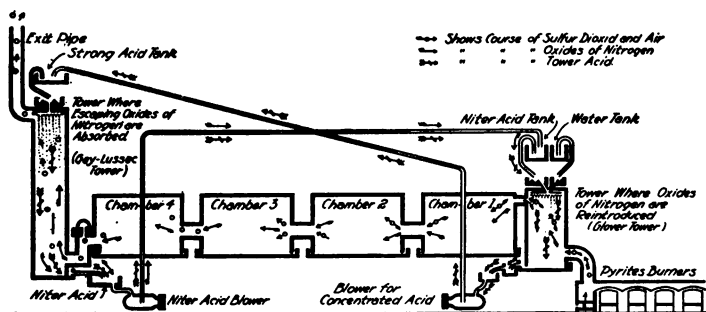
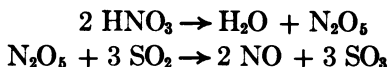


FIG. 71.— Chamber Process for the Manufacture of Sulphuric Acid.
(From Thorp's *Outlines of Industrial Chemistry*.)

nitrogen are poisonous and very offensive, and it would not be permitted to throw them out into the atmosphere even if the manufacturers were willing to waste them. The escaping gas, therefore, is allowed to pass up through a tower filled with tiles over which concentrated sulphuric acid is trickling down. This concentrated acid absorbs the oxides of nitrogen while the uncombined nitrogen passes out from the top. The concentrated acid containing the oxides of nitrogen is pumped to the top of the first-mentioned tower, where by dilution with water it is made to give up its oxides

of nitrogen, which are thus reintroduced into the process to serve again as oxygen carriers.

Under perfectly ideal conditions, a limited amount of nitrogen oxide should serve forever in this process. Practically, a little is continually being lost; this is made up by introducing into the gases from the sulphur burners a little vaporized nitric acid which decomposes and is reduced as follows:



and then the nitrogen oxide continues to act as oxygen carrier. The nitric acid used is generated by allowing sulphuric acid to react with sodium nitrate (Chili saltpeter) placed in a small pot in the flue between the burners and the first tower.

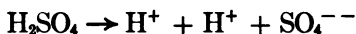


376. Properties of Sulphur Trioxide and Sulphuric Acid. Sulphur trioxide is unlike sulphur dioxide in that it is not a gas. It exists in two modifications, one of which is liquid at ordinary temperature, the other of which is a fibrous white crystalline solid. Both of these forms are very volatile and if left open to the atmosphere evolve dense white fog — due to combining with the water vapor in the air to form sulphuric acid which, condensing to minute droplets of liquid, gives the fog. Sulphur trioxide has a great affinity for water, and if a fragment is thrown upon water it gives a violent hissing sound like the quenching of red-hot iron, owing to the heat released by the reaction.

377. Pure sulphuric acid, H_2SO_4 , is a heavy, oily liquid of specific gravity 1.84. Unlike the sulphur trioxide, from which it is obtained, it is not at all volatile at ordinary tem-

perature. It mixes with water in all proportions and much heat is developed by the admixture. Indeed, sulphuric acid has a good deal of affinity for water. For example, if air or any other gas is slowly bubbled through concentrated sulphuric acid, it is practically freed from water vapor. This is a convenient method for drying gases. Again, if wood or sugar are placed in contact with concentrated sulphuric acid, they are rapidly charred; the hydrogen and oxygen of the wood or sugar have been removed in the form of water, while the carbon is left and gives the charred appearance.

When it is diluted with a considerable amount of water, sulphuric acid is a very strong acid, that is to say, it is largely dissociated into ions:



In virtue of its hydrogen ions, it shows to a marked degree all the typical properties of acids. For example, all metals standing above hydrogen in the electromotive series react with sulphuric acid solution; hydrogen is set free and a sulphate of the metal is left. The sulphates of most of the metals are soluble, so the observed effect of treating a metal with sulphuric acid is that the metal dissolves and hydrogen gas escapes in bubbles.

Sulphuric acid neutralizes bases and basic oxides; sulphates are thereby formed, but there is no effervescence, because the hydroxyl of the base, or the oxygen of the basic oxide, is present to combine with the hydrogen of the acid and retain it in the form of water.

SUMMARY

Sulphur is a typical non-metal. It combines directly with metals and with hydrogen to form sulphides.

Sulphur combines with oxygen to form oxides. These oxides are

acid-forming, which fact is in accord with the non-metallic character of the element sulphur.

Sulphur dioxide when dissolved in water gives sulphurous acid, H_2SO_3 , a weak and very unstable acid. Neutralization of this acid gives a sulphite of the metallic element of the base.

Sulphur trioxide when dissolved in water gives sulphuric acid, H_2SO_4 , a strong and stable acid. Neutralization of this acid gives a sulphate.

Much information concerning the relationships among the most important of the compounds of sulphur is shown in the following table:

SIMPLE COMPOUND	VALENCE OF SULPHUR	ACID	STRENGTH OF ACID	FORMULA OF SODIUM SALT
H_2S	- 2	H_2S	Very weak	Na_2S
S	0			
SO_2	+ 4	H_2SO_3	Weak	Na_2SO_3
SO_3	+ 6	H_2SO_4	Strong	Na_2SO_4

Questions

1. In which of the two great subdivisions of the elements does sulphur belong?

2. The oxides of sulphur yield what type of substance on union with water?

3. Of what practical use is sulphur?

4. What is meant by the popular expression sulphur water, referring to spring water of a certain type?

5. Which of the three elements — oxygen, chlorine, and sulphur — would you regard as the weakest non-metallic element, and why?

6. Explain briefly how the difficulty in getting SO_2 to unite with oxygen is overcome in (a) the contact process, (b) the chamber process of making sulphuric acid.

7. How could you tell by mere inspection whether the acid in a bottle was concentrated HCl or concentrated H_2SO_4 ?

8. In order to appreciate the vast extent of the use of sulphuric acid, try to find in the reference books the value of the acid manu-

factured in the United States in one year. See, also, if you can think of any manufactured article which has not had sulphuric acid used either directly in its manufacture or indirectly in the making of the things used in making the article in question.

9. Compare sulphur with oxygen as to its existing in two or more forms.

10. If a bottle contained sulphuric acid, what effect would it have upon a splinter of wood dipped into it?

11. What weight of sulphuric acid could be obtained from 1000 kilograms of iron pyrite, FeS_2 , if all of the sulphur of the pyrite were utilized?

12. What volume would the sulphur dioxide (figured under standard conditions) obtained as the direct product of burning the 1000 kilograms of pyrite occupy?

13. What property of sulphuric acid makes it useful for drying gases?

14. Why would you not advise trying to dry ammonia gas by bubbling it through sulphuric acid?

CHAPTER XXX

COMPOUNDS OF NITROGEN

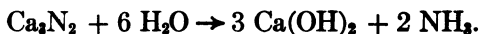
WE have already learned in connection with our study of the atmosphere (Chapter VII) that nitrogen, although it comprises four fifths of the air, is ordinarily an inert element. Only under special conditions does atmospheric nitrogen enter into combination with other elements. When, however, it is once in combination, it enters into further chemical change with great readiness and it is largely on this account that combined nitrogen is of such importance in the chemistry of animal and plant life as well as of explosives.

COMPOUNDS WITH METALS AND WITH HYDROGEN

378. Nitrides. With the very active metals, especially calcium and magnesium, free nitrogen unites with considerable ease to form the nitrides Ca_3N_2 and Mg_3N_2 . This activity, however, plays no part in the economy of nature, first, because calcium and magnesium are too active to be found uncombined, and second, because the ever present oxygen in the air would have the stronger claim upon their combining powers if the metals were ever free to act with the atmosphere.

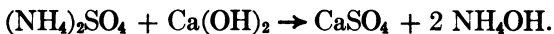
379. Ammonia. It has already been seen that, chemically, hydrogen is classed with the metals. The nitride of hydrogen, or as it is commonly called, ammonia, NH_3 , is one of the very important compounds of nitrogen.

Ammonia can be made from the nitride of calcium or magnesium by treating it with water :



Ammonia can also be made to a slight extent by the direct combination of hydrogen and nitrogen under the influence of the electric spark or of certain catalyzers. If a mixture of three volumes of hydrogen and one volume of nitrogen is subjected to a spark discharge, about 2 per cent of the mixture combines. That the tendency to combine is extremely small is further shown by the fact that if ammonia gas is subjected to the same spark discharge, all but about 2 per cent of it becomes decomposed into the free elements.

The actual source of all the ammonia of commerce is the so-called gas liquor obtained from gas works. Coal is the fossil remains of former vegetation and still contains some of the combined nitrogen that originally existed in the plants. When, in the process of gas manufacture, the coal is subjected to destructive distillation, a large part of the nitrogen passes off as ammonia. In the process of purification, the gas is passed through water; and since ammonia is very soluble in water, the gas liquor retains it and becomes the principal source of this compound. The ammonia of the crude gas liquor is expelled by heat and absorbed in sulphuric acid, forming ammonium sulphate. Crude ammonium sulphate is much used as a fertilizer on account of its nitrogen content. It is also used as a starting point in the manufacture of pure ammonia and pure ammonium salts. It is mixed with calcium hydroxide, whereby the weaker base is set free:



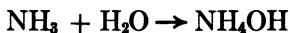
On heating this mixture, ammonia gas passes off, and after proper purification, it is absorbed in water to form ammonia

water, or after drying it is liquefied by compression in steel cylinders for use in refrigerating plants, or it is absorbed in hydrochloric acid to form ammonium chloride (sal ammoniac).

380. Laboratory Preparation of Ammonia. For preparing ammonia in the laboratory, an ammonium salt, usually ammonium chloride, is mixed with a strong base, calcium or sodium hydroxide, and the mixture is heated. Owing to its great solubility, the gas cannot be collected over water. It can be caught over mercury, or for simple experiments it may be run into dry bottles held mouth downward.

381. Properties of Ammonia. Ammonia is a colorless gas of an extremely penetrating but not disagreeable odor. It is dangerous if inhaled in quantity, but diluted with much air it is harmless.

Ammonia is very soluble in water; at 20°C. and atmospheric pressure, one volume of water dissolves 710 volumes of ammonia. The great solubility can be strikingly shown by the same fountain experiment (page 131) that was given to show the extreme solubility of hydrogen chloride. The solution of ammonia is mildly alkaline, due to the formation of ammonium hydroxide, which is a comparatively weak base;



(See Chapter XIX.) It is on account of its alkaline character that ammonia is useful for cleaning purposes.

Dry ammonia gas is easily liquefied. At 20°C., a pressure of 8.4 atmospheres is sufficient to cause its condensation. At atmospheric pressure, a temperature of - 34°C. will cause it to liquefy.

382. Refrigeration. Liquid ammonia is much used in ice machines (see Fig. 72). By means of the engine and pump, the gas is compressed and liquefied. The heat produced by

the compression is removed by passing the ammonia through condenser pipes over which cold water is flowing. The liquid ammonia is now allowed to issue through a small orifice of the expansion valve, into a coil of larger pipe. Heat

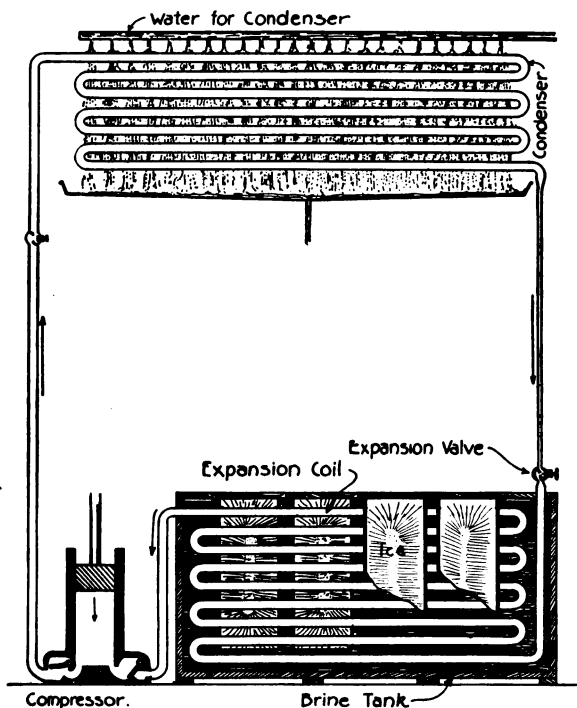
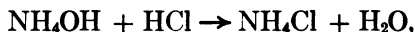


FIG. 72. — Ammonia Refrigerating Plant.

is necessary to cause the liquid to vaporize just as it is necessary to convert water into steam. This liquid ammonia has already been deprived of much of the heat it originally possessed as a gas. In order to vaporize, then, it has to withdraw what heat it can get from its surroundings and hence the

latter are cooled to a very low degree. The expansion pipes are surrounded by a non-freezing brine such as a concentrated solution of calcium chloride (see page 194). This liquid serves as a bath in which to immerse vessels containing the water that is to be converted to ice. Or the liquid itself may be circulated through pipes in the refrigerating plant. As fast as the ammonia vaporizes in the expansion pipes, it is withdrawn by means of the pump and is forced again through the same cycle of operations.

383. Ammonium Salts. Like other bases, ammonium hydroxide is capable of neutralizing acids, as, for example,



and thus we have a series of ammonium salts including the chloride, the sulphate, the nitrate, the carbonate, etc.

Ammonium chloride, NH_4Cl , is commonly known as sal ammoniac, and its solution is much used in bell-ringing electric batteries.

Ammonium carbonate is used in smelling salts. Lumps of the solid salt are covered with alcohol and a little aromatic oil such as oil of lavender is added. The salt is unstable and is continually decomposing into ammonia and carbon dioxide. Thus the smelling salts possess a powerful odor of ammonia.

Ammonium nitrate is used in considerable quantities in explosives. It leaves no solid products, as does the potassium nitrate used in gunpowder; it is serviceable as one of the ingredients of some kinds of blasting powder.

COMPOUNDS WITH OXYGEN

384. A number of compounds of nitrogen and oxygen are known, nevertheless it is a matter of great difficulty to make the two elements combine directly. Ordinarily, they remain

mixed together in the air without the least trace of interaction, but at the high temperature that accompanies the passage of an electric spark they combine to a slight extent. Thus a small amount of nitrogen oxide is formed during thunderstorms in the paths of the lightning flashes. With the rain water it is converted to nitric acid and contributes thus a small share toward fertilizing the soil.

An artificial method of making nitric acid from the air by means of electric sparks has already been referred to in section 75. The success of this process depends largely on being able to withdraw the nitric oxide quickly from the influence of the spark discharge before it can again be decomposed into its elements.

385. There are five distinct oxides of nitrogen; their composition and some of their properties are shown in the following table:

NAME	FORMULA	PROPERTIES
Nitrous Oxide	N_2O	Colorless gas
Nitric Oxide	NO	Colorless gas; unites spontaneously with oxygen to form the red gas NO_2 .
Nitrogen Trioxide	N_2O_3	Very unstable, anhydride of nitrous acid, HNO_2 .
Nitrogen Tetroxide	NO_2 (or N_2O_4)	Brownish red gas; dissolved in water gives a mixture of nitrous and nitric acids.
Nitrogen Pentoxide	N_2O_5	White unstable solid, anhydride of nitric acid.

386. Nitrous Oxide, N_2O , may be prepared by heating ammonium nitrate which decomposes according to the reaction

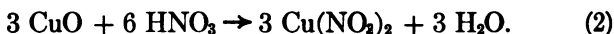
$$NH_4NO_3 \rightarrow N_2O + 2 H_2O.$$

This gas is much used by dentists and surgeons to produce anæsthesia for short operations. Nitrous oxide is a colorless gas, it is somewhat soluble in water, and it has a sweetish taste. It causes a glowing splinter of wood to burst into flame and it supports the combustion of sulphur, phosphorus, and other combustibles with much the same vigor as does pure oxygen; but the animal body is unable to obtain oxygen from it and so it does not sustain life. It is usual to mix it with air when producing anæsthesia so as not entirely to deprive the patient of oxygen.

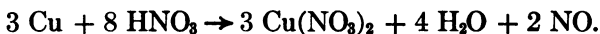
387. Nitric Oxide, NO. For laboratory study, this gas is made by the action of copper on nitric acid. The nitric acid is reduced, that is, it has oxygen taken away from it by the copper:

$$\left. \begin{array}{l} 2 \text{HNO}_3 \rightarrow \text{H}_2\text{O} + 2 \text{NO} + 3 \text{O} \\ 3 \text{O} + 3 \text{Cu} \rightarrow 3 \text{CuO} \end{array} \right\} \quad (1)$$

The copper is thereby oxidized to copper oxide, a basic oxide. We do not see any appearance of this oxide, however, because as fast as it is formed it reacts with the surplus nitric acid to form the salt, copper nitrate:



Reactions (1) and (2) occur simultaneously and are dependent on each other; if their equations are added, the equation for the entire change becomes:



Nitric oxide is a colorless gas and is but slightly soluble in water, with which it does not react. It does not support ordinary combustion, but phosphorus which has been previously kindled will continue to burn in nitric oxide.

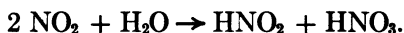
Its most remarkable property is that it combines spontaneously with oxygen in the cold, thereby producing nitro-

gen tetroxide, a deep brownish red gas of a suffocating odor. When, for example, colorless nitric oxide emerges from a delivery tube into the open air, it changes as if by magic into the deep red vapor of nitrogen tetroxide.

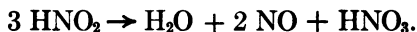
388. Nitrogen Tetroxide, NO_2 , is, as stated, a deep red gas at ordinary temperature. Its odor is suffocating and not altogether dissimilar to that of chlorine. On heating, its color becomes deeper red; on cooling, its color becomes paler until the gas condenses to a pale yellow liquid. This liquid boils at 22°C. and gives the characteristic reddish fumes. At -12°C. it freezes to an almost colorless solid.

The changes of color are believed to be due to a change in the size of the molecule. The red gas is believed to consist of molecules of NO_2 . At 144°C. , the vapor density corresponds to the molecular weight 46 of NO_2 . At lower temperatures the density is higher, indicating a mixture of NO_2 and N_2O_4 molecules. The liquid is supposed to consist entirely of N_2O_4 .

Nitrogen tetroxide is a powerful oxidizing agent, supporting the combustion of most of the ordinarily combustible substances. It dissolves in water and at the same time reacts with it to form a mixture of nitrous and nitric acids:



If the water is warm, the unstable nitrous acid decomposes as follows:

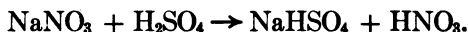


The escaping NO can form further NO_2 when it comes in contact with the air. These reactions play an important part in the process of making nitric acid from the air, for the nitric oxide first formed in the path of the electric spark re-

acts with oxygen to form nitrogen tetroxide and the latter reacts with water.

389. Nitric Acid, HNO_3 , is the most important compound of nitrogen. The great bulk of it is made from crude sodium nitrate, NaNO_3 , which is found in extensive deposits in Chili, South America, and is hence known as Chili saltpeter. The origin of the deposit will be spoken of in a later part of this chapter. Although this deposit is of great magnitude, it is, nevertheless, being used so extensively that it cannot last for a great many years longer, and eventually the world must look to other sources for its nitrate supply, very probably to the electrical method of "fixing" the atmospheric nitrogen.

In the manufacture of nitric acid, Chili saltpeter is treated with concentrated sulphuric acid and the mixture is heated. Nitric acid, being volatile, distils off, while sodium acid sulphate is left in the retort:



The vapor of the nitric acid is passed through air-cooled earthenware or glass vessels in which it condenses to a liquid.

390. Properties of Nitric Acid. Nitric acid, when pure, is a colorless liquid of specific gravity 1.5, but it readily decomposes to some extent, especially if warmed or exposed to the light. Some nitrogen tetroxide is formed, and this colors the liquid yellow or even reddish, and red fumes of it are frequently observed above the liquid in the bottle. Commercial nitric acid has a specific gravity of 1.42 and contains only 60 to 70 per cent of HNO_3 , the rest being water.

One of the most marked properties of nitric acid is its effect on organic matter. It attacks the skin, turning it bright yellow, and when concentrated, it makes severe and deep

burns. Fabrics are at once destroyed if concentrated nitric acid is spilled on them. An ignited piece of charcoal will continue to burn when thrust below the surface of concentrated nitric acid.

Nitric acid is a strong acid in the same sense that hydrochloric and sulphuric acids are strong, that is, it is very highly ionized in its dilute solution and thus furnishes an abundance of hydrogen ions. It has, however, other important properties besides those caused by the hydrogen ions; for example, nitric acid readily attacks copper, silver, and mercury, metals which stand below hydrogen in the electromotive series and which are unacted upon by hydrochloric acid or dilute sulphuric acid. No hydrogen, however, is liberated by the action of nitric acid on these metals; a gas is evolved which is colorless in the bubbles which rise through the liquid but turns red when the bubbles burst and the gas comes in contact with the air. This gas obviously is nitric oxide. The reaction of copper with nitric acid has already been explained in section 387. Nitric acid, coming as it does from the anhydride N_2O_5 , contains an abundant supply of oxygen and is able to release a large part of it very readily. Thus it oxidizes metals. It is most often reduced thereby to nitric oxide:



After oxidizing the metal, nitric acid begins to display its acid function in that it *neutralizes* the basic oxide, forming water and a salt (nitrate) of the metal. In just the same way, hydrochloric and dilute sulphuric acids react with the *oxides* of the metals copper, silver, and mercury and form the corresponding chlorides and sulphates, although the latter acids have no action at all on the uncombined metals.

When metals standing above hydrogen in the electro-

motive series react with nitric acid, there is no reason why hydrogen should not be displaced. Usually, however, it does not escape as such, for nitric acid, being an oxidizing agent, catches the hydrogen in the moment of its formation, when it is particularly active, and oxidizes it to water. A very active metal like magnesium can sometimes, when the acid is dilute, produce hydrogen so copiously that some of it escapes the oxidizing action of the nitric acid and is evolved as hydrogen gas.

Hydrogen is able to react with nitric acid only when it is in the particularly active condition at the moment of its formation at the surface of the metal. A stream of hydrogen formed in a separate generator may be passed freely into nitric acid without the least reaction taking place. Thus whatever hydrogen can get fairly formed and escape from the surface of the magnesium before it is oxidized will be evolved with the other reaction products.

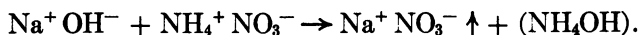
It has already been seen under the preparation of sulphur dioxide that hot concentrated sulphuric acid can react as an oxidizing agent upon copper and that the reduction product of the sulphuric acid is sulphur dioxide in the same way that the reduction product of nitric acid is nitric oxide. Sulphur is a more active element than nitrogen; in consequence, its oxides are more stable, and the oxides, or the acids derived from them, are more difficult to reduce. Cold or dilute sulphuric acid thus is without action on copper, whereas nitric acid reacts when it is both cold and dilute.

391. Reduction of Nitric Acid to Ammonia. The usual reduction product of nitric acid is nitric oxide, NO. If we should imagine the reduction to be carried further, we might expect to obtain free nitrogen. If, however, the reduction gets as far as this, it seldom stops here, but goes a step further.

It may be wondered how this is possible, how anything not possessed can be taken away ! Electrically speaking, we have already seen that addition of positive is equivalent to the taking away of negative, and vice versa. The same is true chemically, and the addition of positive hydrogen is considered reduction as much as the taking away of negative oxygen.

Now when nitric acid is treated with magnesium or zinc or any metal standing high in the electromotive series, there is always the possibility of the setting free of hydrogen. This hydrogen is especially active at the moment of its formation ; and if it finds free nitrogen at the moment of its liberation by the reduction of nitric oxide, it combines with it to form ammonia.

Let us consider the actual experiment of treating zinc turnings with cold dilute nitric acid. The reaction is not so violent as with more concentrated acid, and little or no red fumes of nitrogen dioxide can be seen escaping. We suspect ammonia is formed, but we cannot see it or perceive its odor. In fact, if we reflect a moment we should not expect to find *free* ammonia, for ammonia is basic ; it forms ammonium hydroxide with some of the water present and that in turn reacts with the surplus nitric acid to form ammonium nitrate. With this idea in mind, we can start to show the existence of the ammonia in combination. It is only necessary to add to the solution a stronger base which will liberate the weaker base from its salt :



Then, especially on warming the solution, ammonium hydroxide breaks up into ammonia and water :



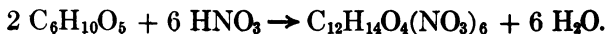
and the odor of the escaping ammonia gas is evident.

The reduction of nitric acid by copper was compared with the similar reduction of sulphuric acid. It is also true of sulphuric acid that it can be reduced to a stage further than the lower oxide or even than free sulphur. When fairly concentrated, warm sulphuric acid is treated with zinc or magnesium, a considerable amount of hydrogen sulphide is obtained among the other gases that escape. The active hydrogen liberated by the metal adds itself to the sulphur.

392. Explosive Compounds of Nitrogen. It has already been stated that nitric acid is a strong oxidizing agent because it is unstable and gives up its oxygen readily. It is also true of nitrogen compounds in general that they are unstable. Many of the compounds of nitrogen are so unstable that they are explosive, that is to say, when they start to decompose they do so with violence.

393. Gunpowder is a mixture of potassium nitrate with powdered charcoal and sulphur. Potassium nitrate, like nitric acid, gives up oxygen readily, and with carbon present to unite with the oxygen, the reaction, if once started, becomes violent within an instant. Nitrogen gas and carbon dioxide, with possibly some carbon monoxide, are gaseous products of the reaction; and the sudden production of a large quantity of these gases added to the expansive effect of the great heat of the reaction accounts for the power of the explosion.

394. Cellulose Nitrate; Guncotton. Most of the modern high explosives are made by the carefully regulated action of nitric acid on some of the organic compounds of carbon. Guncotton is one of these and it is made by the action of a mixture of concentrated nitric and sulphuric acids on pure cotton fiber, which is almost pure cellulose $(C_6H_{10}O_5)_n$.



As seen in the equation, water is one of the products of the reaction; the function of the sulphuric acid is to appropriate this water, which would otherwise accumulate and check the reaction.

When guncotton explodes, a rearrangement of the atoms takes place so that the simpler and much stabler molecules CO, CO₂, H₂O, and N₂ are formed. All of the products are gases and hence no smoke is produced. Guncotton is the basis of modern smokeless powder.

Guncotton is fairly safe to handle, for it is stable enough to withstand considerable heat and shock without exploding. It is customarily fired by means of a detonating cap of mercuric fulminate (Hg(ONC)₂ — also a nitrogen compound). The shock of the explosion of the cap detonates, or explodes, the guncotton. If not detonated but simply ignited with a match in the open, guncotton burns rapidly but usually without trace of explosion.

Lower nitrates of cellulose are made by using less concentrated nitric acid; they are far less explosive than the hexanitate and find use in making collodion, celluloid, and artificial silk. Articles made from them are extremely inflammable.

395. Nitroglycerin, C₃H₅(NO₃)₃, is made by treating glycerin (glycerol) in the same way as cellulose is treated in making guncotton. Nitroglycerin is far more dangerous to handle because it explodes with very slight provocation. Dynamite is made by impregnating diatomaceous earth or other porous material with nitroglycerin. It is far safer to handle than the clear nitroglycerin, and it gives nearly as powerful an explosion.

396. Fixation of Nitrogen by Aid of Bacteria. It was stated in Chapter VII that much atmospheric nitrogen is

continually finding its way into the combined form through the agency of the life processes of certain bacteria which live on the roots of plants belonging to the legume family (peas, beans, lentils, alfalfa, and clover belong to this family). The plants assimilate the nitrogen thus combined and convert it into the complex compounds with carbon, hydrogen, and oxygen which go to make up the protoplasm of the plant cells, the chlorophyll or green coloring matter, etc. The seeds usually are especially rich in nitrogenous substances. Peas and beans thus make valuable food material for men and animals.

The total amount of nitrogen combined by all of the artificial means as well as by the lightning discharges in thunder storms is entirely insignificant in comparison with that fixed by bacterial action.

By plowing under a crop of clover, or other legume, nitrogenous matter can be introduced into the soil, where it becomes finally converted into nitrates. The latter change is accomplished through the oxidizing agency of the air in the presence of the alkaline material of the soil and with the aid of the various bacteria of decay. Nitrogen in the form of nitrates is available for the nutrition of other kinds of plants, such as wheat and oats, which cannot take nitrogen from the air. Unless some such method of getting nitrogenous matter into the soil is adopted, grain and other crops will not thrive after a few years without artificial fertilizers containing nitrogen, such as animal manure or Chili saltpeter (sodium nitrate).

Farmers generally understand the necessity of keeping up the nitrogen content of the soil, and they frequently plant clover, alfalfa, or other legumes, since this method is cheaper than buying expensive sodium nitrate.

397. Origin of Saltpeter Beds. The origin of the Chili saltpeter deposits is not known, but it is generally agreed that the nitrogen is of organic origin, either animal or vegetable. When organic material decays, as in the damp soil of cattle yards, some of the nitrogen is oxidized to nitric acid, which gives nitrates with the alkaline material in the soil; if the surface of the soil is dry, a whitish crust made up of small crystals of potassium nitrate (saltpeter) often forms. In some localities, notably in India, the soil near the villages where, due to imperfect sewage disposal, much nitrogenous matter decomposes, is extracted with water every few years and the nitrates, chiefly calcium and potassium nitrates, are obtained by evaporation.

The Chili saltpeter without doubt arose through the oxidation of vast deposits of nitrogenous organic matter. The soil in that region must have abounded in soda rather than potash or lime. The peculiar formation of the plateau and the absence of rain accounts for the retention of the deposit.

398. The Nitrogen Cycle in Nature. When nitrogenous compounds of either plant or animal origin decay under usual conditions, the carbon is oxidized to carbon dioxide and the hydrogen to water; the nitrogen appears at first in the form of ammonia but this is oxidized partly to free nitrogen which escapes as gas and partly to nitrate. We have thus a complete cycle through which nitrogen passes from the free state in the air, through the combined state in the legume, from the legume to other states of combination in plant and animal matter, and finally through decay back again to the atmosphere. If the legume is eaten by animals the nitrogen is changed into the various nitrogenous substances of the animal body; the decay of either the legumes or of the animal matter

yields in part free nitrogen and in part nitrates, which in the soil serve to nourish other vegetation, which in turn nourishes

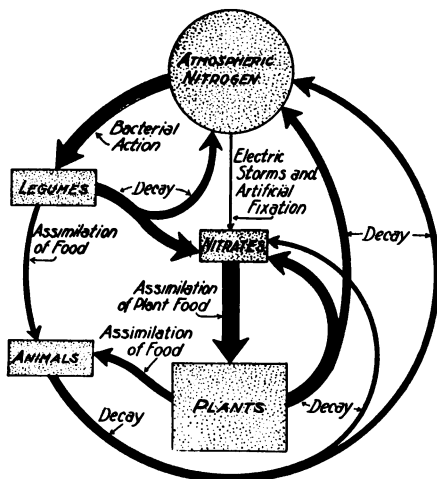


FIG. 73. — Nitrogen Cycle.

animals, or else decays and forms nitrates again or yields back free nitrogen to the air.

In this respect, nitrogen resembles carbon, which was shown in Chapter VI to go through a cycle of changes in which plants and animals and the carbon dioxide of the air play a part.

The amount of nitrogen involved in these changes is smaller than the amount of carbon involved in the carbon cycle. Nevertheless, the same sort of equilibrium is maintained. The relative amounts of combined nitrogen and of uncombined atmospheric nitrogen remain constant because the amount entering combination is just equalled by the amount which is all the time being returned to the atmosphere.

SUMMARY

Free nitrogen is very inactive, but in combination, nitrogen enters freely into reactions and its compounds are of great importance.

Nitrides and Ammonia. Nitrogen combines with the very active metals to form nitrides. The nitride of hydrogen is known as ammonia. It unites with water to form ammonium hydroxide,

a rather weak base. Nitrides other than ammonia are of little practical importance. Ammonia is obtained as a by-product from gas works.

Oxides. Oxygen forms five distinct compounds with nitrogen. Nitrogen pentoxide, N_2O_5 , is the anhydride of nitric acid.

Nitric acid is the most important derivative of the oxygen compounds. It is a strong acid and also a strong oxidizing agent. When it oxidizes other substances, it is, according to conditions, itself reduced to NO_2 , NO , N_2 , or even in extreme cases to NH_3 . Nitric acid is obtained principally by treating Chili saltpeter, $NaNO_3$, with sulphuric acid.

Explosives. Oxygen compounds of nitrogen and their derivatives are very unstable and form the basis of all the common explosives.

A natural cycle of changes is undergone by nitrogen in much the same manner as by carbon. The decay of nitrogenous material returns to the atmosphere an amount of nitrogen just equalled by that entering combination chiefly under the influence of leguminous plants.

Questions

1. When powdered magnesium is heated in a crucible with loosely fitting lid and water is added to the residue after cooling, some ammonia is set free, as can be told by the odor. Account for the formation of the ammonia.

2. Explain the use of anhydrous ammonia in making artificial ice.

3. A flask is filled with a colorless gas, but when the stopper is taken out the gas in the neck of the flask turns brown. What is the gas?

4. How does the action of nitric acid on copper differ from the action of hydrochloric acid on zinc?

5. Write the reaction of nitric acid with silver, remembering that the formula of silver oxide is Ag_2O .

6. Show by equations how ammonium nitrate can be one of the products of the action of nitric acid on zinc. What gaseous reduction products may escape at the same time that the ammonium nitrate is being formed?

7. Why do farmers sometimes plant clover only to plow it under without harvesting the crop?

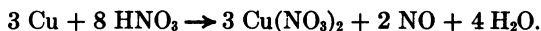
8. What weight of calcium hydroxide is necessary to react with 100 grams of ammonium sulphate in the preparation of ammonia?

9. What volume would the ammonia gas occupy under standard conditions?

10. What weight of 28 per cent ammonia solution would be obtained?

11. What volume would this solution occupy if its specific gravity is 0.90?

12. What weight of 70 per cent HNO_3 should be taken to just dissolve 190.8 grams of copper?



13. At standard conditions, what volume of NO gas would be evolved in question 12?

14. With what volume of air (20 per cent oxygen) should this nitric oxide be mixed in order to change it all to NO_2 ?

15. Formulate as well as you are able the reactions for the explosion of ordinary gunpowder and of smokeless powder. Explain why the former produces smoke and the latter does not.

16. Heat is evolved when N_2O decomposes into nitrogen and oxygen. Consider this fact and explain why N_2O should support combustion practically as well as pure oxygen.

CHAPTER XXXI

THE HALOGEN FAMILY; THE PERIODIC SYSTEM

399. Natural Families of the Elements. With the eighty or more elements which are known to exist, it would be strange if there were not resemblances between some and dissimilarities between others. A comparison of all the elements has shown that what would thus be expected is amply fulfilled by the facts, for the elements seem to arrange themselves naturally into families, and the elements within a family show to a marked degree certain traits which are characteristic of that family. One of these families, the so-called *halogen* family, forms the subject matter for this chapter.

The best-known element of this family is chlorine. The other elements are fluorine, bromine, and iodine. All four elements form salts which are extremely alike in character. Thus the sodium salts of fluorine, bromine, and iodine are very similar to common salt, which is the sodium salt of chlorine, and hence the name halogen, which comes from the Greek and means salt-former.

It is recalled that chlorine is a gas with a very disagreeable odor, that it unites readily with metallic elements and forms salts. Fluorine, bromine, and iodine also are all possessed of a most disagreeable odor. They all combine easily with metals and give salts which strongly resemble the chlorides. Whenever the chloride of a metal is colorless, the fluoride, bromide, and iodide of that metal are apt to be also colorless.

Most of these salts are soluble in water. The hydrogen compounds are all soluble in water and form acids, namely hydrofluoric acid, hydrochloric acid, hydrobromic acid, and hydriodic acid. All four elements possess the same valence in their compounds with metals and with hydrogen, namely, the valence one. Hence they can mutually replace each other, atom for atom, in their compounds without materially altering the nature of the compound. Thus the symbols of the acids are:



and of the sodium salts are:



FLUORINE

400. Uncombined fluorine is a gas like chlorine. It possesses a similar color and odor, the color being a paler yellow, whereas the odor is even more offensive. Fluorine is a more active element than chlorine; it is in fact the most energetic non-metallic element known. It reacts spontaneously with all of the ordinary substances of which the vessels used in preparing and collecting gases are made, and for this reason it defied for a long time all attempts to obtain it in the uncombined condition.

It reacts vigorously with water, setting oxygen free and forming hydrofluoric acid. It combines spontaneously and with intense energy with most of the elements, including sulphur, phosphorus, and the metals. Gold and platinum vessels resist it to a sufficient extent so that they may be used as containers in preparing it.

Fluorine has a strong action on glass. It attacks organic compounds, such as wood, rubber, paraffin, and oil, with violence, so that they are often inflamed. Fluorine enters

into chemical combination with the silicon of the glass and with the hydrogen of the organic substances.

401. Preparation. Fluorine being the most active non-metallic element, there can be no other element which can displace it from its compounds, after the manner in which the more active oxygen of oxidizing agents can displace the less active chlorine from hydrochloric acid :



Our only recourse, then, is to drag fluorine apart from the element with which it is in combination by means of the electric current.

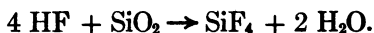
Moissan, a noted French chemist, succeeded in 1886 in obtaining uncombined fluorine by passing an electric current through a solution of potassium fluoride in dry liquid hydrogen fluoride contained in a platinum U-tube. Hydrogen was evolved at the negative electrode, fluorine at the positive electrode. The fluorine was passed through platinum tubes and was caught in platinum vessels by displacement of air. It is perhaps needless to say that the preparation of fluorine has not often been repeated.

402. Occurrence. Fluorine is found in nature as a constituent of certain minerals, the most important of which is fluorspar (CaF_2). Unfortunately, the phosphate rock, $\text{Ca}_3(\text{PO}_4)_2$, which is used in making fertilizer, often contains some calcium fluoride; the hydrofluoric acid evolved when the rock is treated with sulphuric acid is a menace to the health of the workmen.

403. Hydrofluoric acid. The most important compound of fluorine is hydrogen fluoride, or hydrofluoric acid, HF. This is prepared much after the manner of hydrochloric acid : Fluorspar is treated with concentrated sulphuric acid in lead

retorts. On distillation, the gaseous hydrogen fluoride passes off, and this is passed into water in lead bottles, where a solution of hydrofluoric acid is obtained. This acid is put on the market in bottles of gutta percha or wax because glass is attacked by it.

Hydrofluoric acid does not attack rubber, wax and paraffin as does uncombined fluorine, because the element is already in combination with hydrogen in the acid; but hydrofluoric acid does attack glass. It reacts with the silicon dioxide, which is one of the principal components of glass:



Silicon tetrafluoride, SiF_4 , is a gaseous substance and escapes from the sphere of action.

One of the most important uses of hydrofluoric acid is for etching glass. The aqueous acid dissolves away the glass and leaves a smooth hollowed surface, but gaseous hydrogen fluoride, although it acts chemically in much the same way, leaves a roughened surface which has the appearance of ground glass. The object to be etched is coated with wax and the design is drawn in the wax, making bare the glass in the desired places. Then the whole is exposed to hydrogen fluoride gas and the design is etched. The graduations on our glass measuring vessels are usually marked in this manner.

Hydrofluoric acid is extremely poisonous; its vapor is dangerous to breathe, and even small drops of the solution cause painful ulcerated sores on the flesh.

BROMINE

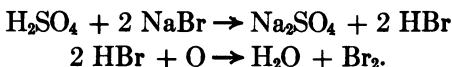
404. Uncombined Bromine is a dark red liquid which freezes at -7°C . and boils at 63°C . It is about three times as heavy as water. It evaporates very easily at ordinary tem-

perature, and when a bottle is partly filled with liquid bromine, the upper part is always filled with red bromine vapor. The odor of bromine is similar to that of chlorine and it is fully as offensive, — in fact, its name is derived from the Greek word meaning stench.

The chemical reactions of bromine are much the same as those of chlorine, except that they are generally less vigorous. If powdered antimony is thrown into a jar of bromine vapor, it does not flame up spontaneously as it does when thrown into chlorine. If, however, the antimony is dropped into a little liquid bromine in a test tube, it shows a vigorous reaction.

If a mixture of hydrogen and bromine vapor is passed through a heated tube, the elements combine quietly and form hydrogen bromine, but there is no explosion as when a mixture of hydrogen and chlorine reacts (see page 169).

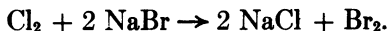
405. Occurrence and Preparation. Wherever chlorine occurs in nature, bromine almost invariably appears, but only in extremely small amounts. Thus in the brine from salt wells there is usually a small amount of bromine. After these brines have been evaporated and all the salt possible has been crystallized out, the "mother liquor" still contains all the bromine as sodium bromide (or magnesium bromide). The bromine is then liberated from this compound, much as chlorine is liberated from common salt, namely, by the addition of sulphuric acid and an oxidizing agent:



The bromine is distilled off and condensed as the dark red liquid of commerce.

It has been said that chlorine is a more active element

than bromine. Once in combination, it is more difficult to get it out of combination. It is, therefore, quite as one would expect, that when a bromide is treated with chlorine the bromine is forced out of combination while the chlorine enters in its place :



Use is often made of this fact in the manufacture of bromine. Chlorine gas is blown into the hot colorless sodium bromide liquor, where it is absorbed, while the red vapors of bromine emerge and are blown along to the condensing tubes.

406. Hydrobromic acid. Hydrogen bromide is a substance most strikingly like hydrogen chloride in all its properties. It is a colorless gas of an irritating odor. It is extremely soluble in water and in aqueous solution is known as hydrobromic acid, an acid which is fully equal in strength to hydrochloric acid.

407. Uses of Bromine and of Bromides. Bromine is of more practical use than fluorine, although it is not nearly so much used as chlorine, whose compounds are more abundant. Most of the uses of free bromine depend on its being an oxidizing agent, but a somewhat less vigorous one than chlorine. It finds use in the preparation of many of the coal tar dyes.

Some of the bromides are used as sedatives in medicine. Silver bromide is the light-sensitive substance of most photographic plates and films and of much of the photographic paper. Silver bromide, like the chloride and iodide, is extremely insoluble in water.

IODINE

408. Uncombined Iodine is a dark, blue-black solid substance which is usually formed in thin platelike crystals.

It is so dark colored that it appears opaque when seen in a mass, but in thin plates it is found to be as transparent as an equally deep colored piece of glass. Like bromine, iodine is very volatile, and if a small grain of it is warmed in a test tube, the tube becomes filled with the most beautiful violet vapor of iodine.

Iodine is a noteworthy substance on account of its great volatility; when it is warmed in an open dish, as for example on a watch glass, it all passes directly from the solid state to the vapor state without first melting. If, however, a considerable amount of iodine is heated in a narrow-necked flask, it melts at 114°C . and the liquid iodine boils at 184°C .

The chemical reactions of iodine are very similar to those of chlorine and bromine, except that they are much less vigorous than the latter. Iodine can without difficulty be made to combine with the more active of the metals, but the combination is not attended with evidence of a violent reaction as is the case with chlorine and to a lesser extent with bromine.

409. Uses of Iodine. Iodine dissolved in alcohol or in a solution of potassium iodide finds extensive use in medicine. Concentrated, it is used as a counter irritant, — being painted on the skin over a bruise or other injury to bring the blood more abundantly to the surface and hence relieve the congestion beneath. In a more diluted condition iodine solutions make a valuable antiseptic wash for wounds. The iodides are also used in medicine.

Hydrogen and iodine can be made to combine to a slight extent when a mixture of the two is passed through a heated tube, but the combination is far less complete than that of hydrogen and bromine. Hydrogen iodide is a colorless gas like hydrogen chloride and hydrogen bromide; like them,

also, it is very soluble in water and its solution is a strong acid, — hydriodic acid.

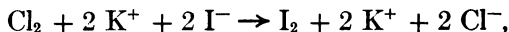
410. Occurrence and Preparation. Although it is a well-known and a frequently used element, iodine is not at all abundant in nature. It is found in extremely minute amounts in the ashes of seaweeds and in Chili saltpeter. It is obtained from the mother liquor when the latter is crystallized, much as bromine is obtained from the mother liquor when common salt is crystallized (see page 381). The quantity of iodine in the earth is about as many times less than that of bromine as that of bromine is less than that of chlorine.

411. Displacement by other Halogens. Iodine is the least active of the halogens; it shows the least energy when it enters into combination with metallic elements, it is correspondingly the most easy to separate from its compounds. Both chlorine and bromine (and, of course, fluorine) are able to displace it from its compounds,

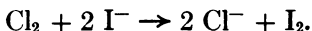


Thus if a little chlorine is bubbled into a colorless solution of potassium iodide, the iodine is displaced according to the foregoing equation, the liquid becomes dark colored in consequence, and flakes of solid iodine are precipitated out when enough has been set free to more than saturate the solution.

If the above equations are written in ionic form :



it is seen that the metal ion is unchanged and may be cancelled from the equation :



The reaction appears thus to be merely a matter of the more active negative element withdrawing electric charges from the less active element.

Iodine has a very characteristic property of giving, with starch, an intense blue color. When so small an amount of iodine is set free in solution that its own color is scarcely perceptible, if a little cooked starch paste is added, a marked blue color may be seen.

Combined iodine does not give this test. A colorless mixture of potassium iodide and starch can therefore be prepared; and strips of paper soaked in this mixture and dried are useful in testing for chlorine and bromine.

THE PERIODIC CLASSIFICATION OF THE ELEMENTS

412. In the living world, scientists have found that animals and plants can be classified into families. For example, the domestic cat, the wild cat, the leopard, the tiger, and the lion are placed in one family because they all possess certain family characteristics in their physiological structure and their habits of life. On the other hand, the horse, the donkey, and the zebra are placed in another family because they have family characteristics markedly different from those of the cat family.

A similar sort of classification can be applied in the inorganic world, and even the elements themselves fall into natural groups or families of which the halogen family is a striking example. The Russian chemist, Mendelejeff, first clearly perceived and showed that all the elements could be arranged according to a definite system, — which we know as the periodic system.

He arranged all of the elements in a regular order, starting

with the one of lowest atomic weight and proceeding in the order of increase of atomic weight, and he thus showed that certain special properties recur at fairly regular intervals. The elements in which these properties recur are the ones which, like the halogens, fall into the same family.

The lightest known element upon this earth is hydrogen, to which we give, arbitrarily, the atomic weight of one. This element seems to stand rather by itself, but the next eight elements, with their atomic weights, are shown in the following table:

HELIUM (4)	LITHIUM (7)	BERYLLIUM (9)	BORON (11)	CARBON (12)	NITROGEN (14)	OXYGEN (16)	FLUORINE (19)
Inert gas, no compounds	Alkali metal resembling sodium, melts easily	Light metal much like magnesium, melts at bright red heat.	Solid non-metal, infusible	Solid non-metal, infusible	Inert gas, non-metal	Active gas, non-metal	Extremely active gas, non-metal
	Li ₂ O	BeO	B ₂ O ₃	CO ₂ H ₄ C	N ₂ O ₅ H ₃ N	H ₂ O	HF

It is seen from the few properties enumerated in the table that these elements are very unlike each other in their physical properties and in the kind of compounds that they form. Next to helium, the absolutely inert gas, comes the very active metallic element lithium. The next element is a metal, but not as active a one as lithium. The next is not a metal, although it is not a pronounced non-metal. With each successive element, the non-metallic properties grow

more marked, until in fluorine we find the most active of all the non-metallic elements.

The next element beyond fluorine is neon, but we do not place this to the right of fluorine, but rather we begin a new series, and place neon beneath helium, for, like the latter, it also is an absolutely inert gas. Next comes sodium, which is a sister element to lithium and therefore fits naturally into the position below the latter.

The complete series of the eight elements following fluorine is shown in the next table, and an inspection shows at once a marked similarity in every case between the elements

NEON (20)	SODIUM (23)	MAGNESIUM (24)	ALUMINIUM (27)	SILICON (28)	PHOSPHORUS (31)	SULPHUR (32)	CHLORINE (35.5)
Inert gas, no compounds	Alkali metal, melts easily	Light metal, melts at red heat	Light metal, melts at red heat	Solid non-metal, melts at white heat	Solid non-metal, melts easily	Solid non-metal, melts and vaporizes easily	Extremely active gas, non-metal
	Na_2O	MgO	Al_2O_3	SiO_2 H_4Si	P_2O_5 H_3P	SO_3 H_2S	Cl_2O_7 HCl

that occupy the corresponding places. Sulphur corresponds to oxygen in position, and we have already learned that sulphur and oxygen are interchangeable atom for atom in the sulphides and oxides. Chlorine corresponds to fluorine, and we have already discovered their strong family resemblance in the first part of this chapter.

The next element to chlorine is argon, another inert gas which falls naturally into the position below neon; next is

potassium, an alkali metal which falls naturally below magnesium. As we go on in this next series, however, we find that the seventh and eighth elements, chromium and manganese, respectively, are heavy *metals* and do not correspond in properties with oxygen and sulphur, fluorine and chlorine, respectively. In fact, we now have to go through a series of eighteen, instead of eight, elements before we come to bromine, the next member of the halogen family. The periods, after the first two, lengthen out to eighteen instead of eight elements; and the fourth as well as the third period contains this number of members (if we are willing to take one for granted which has not yet been discovered, but which we feel sure must exist and probably will some day be found), and the eighteenth element beyond bromine is iodine, another of the halogen family.

This brief discussion of the periodic system shows that there must be some regular law according to which the elements have been formed — perhaps *are* still being infinitely slowly formed. So far we have taken up the study of about twenty only of the most common of the elements, and it is therefore impossible to discuss in detail all of the wonderful analogies brought to light in the periodic system.

A complete table of the periodic classification is given on the opposite page, and it is possible to tell a great deal about the properties of any element, of which we have no other previous knowledge, simply by observing the position it occupies in the table. It will strongly resemble the other elements in its family and particularly those lying nearest to it.

Thus we can conclude that krypton and xenon, Kr and Xe, which appear in column 0, are inert elements like argon, and thus are capable of forming no compounds whatever. Rubidium and caesium, Rb and Cs, in Family A, Group I,

PERIODIC ARRANGEMENT OF THE ELEMENTS

GROUP	0	I	II	III	IV	V	VI	VII	VIII
Highest Oxide	E	E ₂ O	EO	E ₂ O ₃	EO ₂	E ₂ O ₅	EO ₃	E ₂ O ₇	EO ₄
Family		A	A	A	A	A	A	A	
First Short Period	He (4)	Li (7)	Be (9.1)	B (11)	C (12)	N (14)	O (16)	F (19)	
Second Short Period	Ne (20)	Na (23)	Mg (24.3)	Al (27.1)	Si (28.3)	P (31)	S (32.1)	Cl (35.5)	
First Long Period	A (39.9)	K (39.1) Cu (63.6)	Ca (40.1)	Sc (44.1) Zn (65.4)	Ti (48.1) Ge (72.5)	V (51.2) As (75)	Cr (52) Se (79.2)	Mn (54.9) Br (79.9)	Fe (55.9) Co (59.0) Ni (58.7)
Second Long Period	Kr (83)	Rb (85.5) Ag (107.9)	Sr (87.6) Cd (112.4)	Yt (89) In (114.8)	Zr (90.6) Sn (119)	Cb (93.5) Sb (120.2)	Mo (96) Te (127.5)	— I (126.9)	Ru (101.7) Rh (102.9) Pd (106.7)
Third Long Period	Xe (130.2)	Cs (132.8) Au (197.2)	Ba (137.4) Hg (200)	La (139) Tl (204)	Ce* (140.3) Pb (207.1)	Ta (181) Bi (208)	W (184)	—	Os (190.9) Ir (193.1) Pt (195)
	Nt (222.4)		Ra (226.4)		Th (232.4)		U (238.5)		

* Between Cerium and Tantalum lie a number of elements which are very similar to each other in properties and which, together with Yttrium, Lanthanum, and Cerium, which they much resemble, constitute the so-called rare earth elements.

are very active alkali metals like sodium and potassium. Strontium, barium, and radium, Sr, Ba, and Ra of Family A, Group II, are active alkaline earth metals like calcium. Selenium and tellurium, Se and Te, of Family B, Group VI, are non-metals resembling sulphur.

The periodic classification has been of very great use in inspiring and directing search after new elements. It is also very useful because of the means which it affords of enabling us to remember the properties of the elements by groups. Thus if one knows well the general properties of the halogen family, he has to remember but little more in order to be quite familiar with the properties of each member of that family.

SUMMARY

The halogen family of the elements includes fluorine, chlorine, bromine, and iodine which show marked resemblances to each other in their physical and chemical properties and constitute a natural family of the elements.

Fluorine is the most active of the halogens, in fact, of all the non-metallic elements. Hence it cannot be displaced from its compounds by any other non-metallic element. It can be prepared only by electrolysis.

Hydrofluoric acid resembles hydrochloric acid in its properties. It is prepared from calcium fluoride in the same manner as hydrochloric acid is made from sodium chloride. Its most remarkable property is its ability to attack glass and it finds use in etching glass.

Bromine resembles chlorine but is denser (being liquid at ordinary temperatures), darker, and less active. Chlorine displaces it from its compounds.

Hydrobromic acid, like hydrofluoric, resembles hydrochloric acid.

Iodine is solid at ordinary temperatures but readily volatilizes if warmed. It resembles the other members of the family, but it is the least active and can be displaced from its compounds by any one of the others.

Hydriodic acid resembles hydrochloric acid, but it is less stable.

Periodic Classification. With increasing atomic weights of the elements, the properties undergo regular cycles of changes. Given properties recur periodically at the same point in each cycle. The credit belongs to Mendelejeff for arranging the elements according to the periodic classification in which the members of a given family occupy similar positions in the succeeding periods.

Questions

1. In what respects do the elements of the halogen family resemble each other most strongly?

2. Explain the principal use of hydrofluoric acid.

3. Compare the behavior of each of the halogens with hydrogen.

4. How would you test a material to see if it contained free iodine? combined iodine?

5. How would you test a sweet potato for presence of starch?

6. Explain the test given by the potassium iodide-starch paper for free chlorine or bromine.

7. How might a study of the periodic table of the elements show what elements, not yet discovered, may sometime be found in the earth? Could the properties of such elements be foretold?

8. What weight of iodine is contained in 1000 grams of potassium iodide?

9. What weight of chlorine is necessary to just displace the iodine from 1000 grams of potassium iodide?

10. What volume of chlorine (standard conditions) corresponds to the weight taken in Question 9?

11. How large a flask may be filled with pure bromine vapor at atmospheric pressure if 5 c.c. of liquid bromine, sp. grav. = 3.19, is poured into the flask which is then immersed in boiling water?

12. Write equations for the following cases: (a) $\text{CaF}_2 + \text{H}_2\text{SO}_4$ (hot concentrated); (b) $\text{MnO}_2 + \text{HBr}$ (see chapter on chlorine); (c) $\text{Cu} + \text{Br}_2$; (d) $\text{CuO} + \text{HBr}$.

13. Write ionized equations for the following:

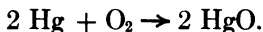
(a) $\text{KI} + \text{Cl}_2$; (b) $\text{KBr} + \text{AgNO}_3$; (c) $\text{CuBr}_2 + \text{Cl}_2$;
(d) $\text{HI} + \text{Zn}$; (e) $\text{HBr} + \text{NaOH}$; (f) $\text{HBr} + \text{CuO}$.

CHAPTER XXXII

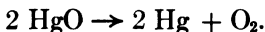
REVERSIBLE CHEMICAL REACTIONS; CHEMICAL EQUILIBRIUM

413. Reversible Reactions. It has probably not escaped the attention of the thoughtful reader that many of the chemical reactions studied in the foregoing chapters can under certain conditions be made to reverse themselves, that is to say, the products of the ordinary reaction may be made to interact with each other to give back again the substances originally started with. Reactions which are thus capable of proceeding in opposite directions under different conditions are known as *reversible reactions*.

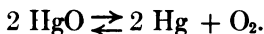
414. Reversal effected by Varying the Temperature. When mercury is heated moderately in the presence of oxygen or air, it combines with oxygen, and the red oxide is formed:



When, however, as in the course of the preparation of oxygen (page 29), mercuric oxide is more strongly heated, it decomposes into mercury and oxygen:



If it is desired to draw attention to the reversibility of a reaction, the equation is written with a double arrow, one pointing in each direction:



It is often the custom to make one arrow heavier to indicate the direction of the prevailing reaction.

Such reactions as the one just mentioned, in which the direction may be changed by change of temperature, are very frequent.

It may seem a little perplexing that moderate heat appears to be necessary to induce mercury and oxygen to combine, although a more intense heat causes decomposition. As a matter of fact, the lower the temperature the greater is the tendency of mercuric oxide to form in comparison to its tendency to decompose. All reactions take place more rapidly when hot, more slowly when cold, and the particular reaction of the formation of mercuric oxide takes place so slowly at room temperature that it is not perceptible.

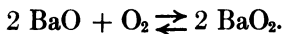
Heat is a form of energy which works most often in opposition to chemical affinity. The affinity between mercury and oxygen is not extremely great, — mercury being one of the least active metals, — and only a rather moderate degree of temperature is necessary to overcome this affinity and decompose the compound. This temperature is only a little higher than the temperature necessary to make the reaction of formation perceptible, and thus we explain the fact that mercury and oxygen are apparently indifferent to each other at room temperature, that they unite at a slightly elevated temperature, but that they break apart again at a still higher temperature.

What has been said of mercuric oxide is true of almost every chemical compound. Take, for example, water: At ordinary temperatures, hydrogen and oxygen gases do not react perceptibly when mixed together. Raise the temperature, however, to a point where the reaction commences to be appreciable, and a very violent explosion ensues. The water vapor formed is ordinarily a very stable compound, but raise it to 2000° C. (a temperature higher than that of

the hottest part of the Bunsen flame) and it is decomposed to a slight degree into hydrogen and oxygen ; raise the water vapor to 3000° C. and it is entirely decomposed.

Very few compounds exist that cannot be decomposed into their elements by a sufficiently high degree of heat. Calcium and oxygen have a tremendous affinity for each other, and calcium oxide can withstand the temperature of the oxyhydrogen flame (about 2500° C.) without decomposition. In the sun, however, where the temperature is estimated to be about 6000° C., calcium oxide does not appear to exist, for the spectroscope shows us the presence of uncombined calcium vapor.

415. Reversal caused by Change of Concentration. It is possible to change the direction of chemical reactions, not only by altering the temperature, but by varying the concentration of one or more of the reacting substances. The effect of concentration is well illustrated by a process which was much used in the commercial preparation of oxygen before the liquid air method was perfected, and which is based on the reversibility of the reaction between barium oxide and oxygen on the one hand, and barium peroxide on the other hand :



Although it is true that barium oxide will take on oxygen from the air at a moderate red heat, whereas barium peroxide will decompose into barium oxide and oxygen at a white heat and the direction may thus be reversed by changing the temperature, it was found in practice to be more economical to maintain a constant temperature at 700° C. and to effect the change by altering the concentration of the oxygen in the tubes containing the solid oxide.

According to this process, air is first forced under high

pressure into the tubes and the concentration of oxygen is thus increased, thereby causing the oxygen to combine with barium oxide and form the peroxide. The nitrogen which is left is allowed to escape through a valve at the further end of the tubes, and fresh air is continually pumped into the tubes. When all of the barium oxide is changed to barium peroxide, the pumps are reversed so as to produce a vacuum in the tubes. The concentration of the oxygen is thus reduced and the barium peroxide begins to decompose and continues to give off oxygen until only the original barium oxide is left. The oxygen thus pumped out is forced under pressure into the steel cylinders in which it is marketed, and the barium oxide left in the tubes is ready to be again carried through the same cycle of operations.

416. Chemical Equilibrium. Barium peroxide has a tendency to decompose at 700°C . and we can actually observe that it gives off oxygen at this temperature into a vacuum or into a space containing very little oxygen. A theory of reversible reactions and of chemical equilibrium has been worked out; and in the light of this theory, we believe that at 700°C barium peroxide decomposes and gives off oxygen just as rapidly into a space already filled with oxygen as into a vacuum. Only we cannot observe it under these conditions, for the reverse reaction, that is, the formation of barium peroxide, is now progressing more rapidly than its decomposition.

When no oxygen is present, this reverse reaction cannot take place, and we observe only the decomposition of the peroxide. When oxygen is present, it reacts with the barium oxide and with a rapidity that depends on its concentration. So if there is but little oxygen in the chambers with the barium oxide, the rapidity of the combination is not great. The decomposition of the barium peroxide is progressing all the

time, but the recombination (which we regard as altogether another reaction) is inappreciable. So when the exhaust pumps are working and the amount of oxygen is being kept low, we observe only the decomposition of the barium peroxide, which is then the predominating reaction.

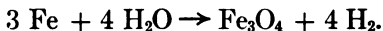
If the amount of oxygen in the chambers is increased, the rapidity of the recombination is increased. When a point is reached at which the rapidity of recombination is equal to the rapidity of decomposition, the two opposed reactions balance each other, because the sum of their effects is zero. No change, therefore, can be observed to take place, although we believe that the two opposite reactions are really taking place.

If the amount of oxygen in the chambers is increased still further, the reaction of combination begins to outdistance that of decomposition, and the amount of barium peroxide increases. This is the condition that prevails in the process when air is pumped under high pressure into the chambers in order to build up the barium peroxide.

The point at which the rate of the opposed reactions is equal and at which there is therefore no apparent change is known as the *point of equilibrium*. Such an equilibrium point exists for every reversible reaction, and if a system is left to itself either one reaction or the other will predominate until the equilibrium point is reached, after which the two reactions will continue to mutually undo the effects of each other.

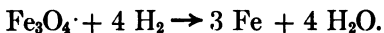
417. Another Reversible Reaction and its Equilibrium Point. Let us consider one more example of an easily reversible reaction and let us also consider the conditions which lead to a state of equilibrium when the rate of the forward reaction is just equaled by the rate with which the products of this reaction interact to form again the original substances.

It will be recalled that one of the practical methods of preparing hydrogen gas is to pass superheated steam through a tube containing iron turnings kept at a high temperature. The oxide of iron, Fe_3O_4 , is formed and hydrogen is left uncombined.



The hydrogen passes out of the further end of the tube together with a large amount of undecomposed steam. The latter condenses to liquid water when it is cooled, whereas the hydrogen passes along for use.

It is a well-known fact that iron oxide may be reduced to metallic iron if it is heated in a tube through which hydrogen is being passed :



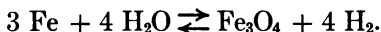
The water vapor so formed is swept along by the current of hydrogen and drops of liquid water may be seen to condense beyond in the cool part of the tube.

The two reactions just discussed are the exact reverse of each other. In the first of them, an abundant supply of steam is kept continually in contact with the iron. This naturally tends to react, but the product of this reaction, the hydrogen, is not allowed to remain to reduce the iron oxide again, but is swept along out of the way by the excess of the steam.

In the second of the reactions, the reverse is true. Hydrogen is supplied abundantly and has every opportunity to react with the iron oxide. The water vapor formed is given no chance to oxidize back any of the reduced iron, for it is swept along out of the way by the excess of hydrogen.

In neither of these cases is there any chance given to attain an equilibrium, for one of the reaction products is in each case removed as fast as it is formed.

If, however, iron filings are heated in a sealed bulb with some water vapor, the hydrogen formed remains in the field of action and it begins at once to reduce the oxide. As the amount of hydrogen increases, the rate at which it reduces the iron oxide increases, and finally a point is reached at which the rate of reduction is just equal to the rate of oxidation of iron. This is the equilibrium point for the reversible reaction :



If, on the other hand, we start with iron oxide and pure hydrogen in the bulb, the right-to-left reaction begins at once, but as the water vapor accumulates, the rate of the left-to-right reaction increases until equilibrium is reached from this side.

The point of equilibrium for this, or any, reaction is exactly the same from whichever side it is approached.

418. The Mass Law. The primary cause of all reactions is chemical affinity, that is, the mysterious force of attraction which holds compounds together ; but, as we have just seen, the direction of a reaction and its point of equilibrium are strongly influenced by two other factors, namely, temperature and concentration of the reacting substances and reaction products.

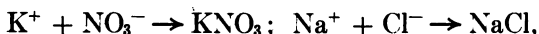
At a constant temperature, the course of many reactions can thus be determined by fixing the concentration of the substances involved. The term " mass " is used a great deal in this connection instead of the term concentration, and the principle just stated is known as the *mass law*. It is a law of the most far-reaching importance and to-day no efficient chemist undertakes to carry through a chemical process without studying it fully from the viewpoint of the mass law.

Some of the applications of the mass law in complex mixtures become very involved, but in its essence, the law is as simple as the law of mass plays on a football field, — that the side which gets the most men and the strongest men into the action succeeds in pushing the ball towards the opponents' goal.

419. Formation of Precipitates. When solutions of two salts are mixed together, there is oftentimes very little evidence of reaction. For example, if a solution of potassium chloride is poured into a solution of sodium nitrate, both salts are ionized :

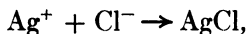


A glance at these formulas shows that reactions to form two new salts,



are possible, but these are both reversible reactions and the two new salts have a strong tendency to remain in the ionized condition (see page 307). Consequently, there is but very little reaction. If, however, it were possible to remove one of these new salts from the sphere of action as fast as it formed, it could no longer enter the reverse reaction and we should find the forward action prevailing.

When a salt is insoluble and falls out of the solution in the form of a precipitate, it is effectively removed from the sphere of action. Thus when potassium chloride and silver nitrate solutions are mixed, the reaction,

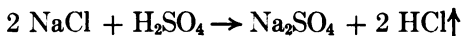


becomes possible because silver chloride is extremely insoluble; as fast as it is formed, it drops from the solution

as a white precipitate. There being practically no silver chloride left in the solution to dissociate again into the ions, the reaction in this direction is lacking and consequently the reaction in the direction of the formation of the salt becomes complete.

The foregoing is but one illustration of the general rule: *When ionized substances are mixed in solution, a reaction will take place if any one of the possible products is insoluble. The reaction will run the more nearly to completion the more insoluble the new compound is.*

420. Formation of Volatile Products. In the preparation of hydrochloric acid (page 129), concentrated sulphuric acid is allowed to react with solid sodium chloride and the reaction

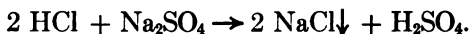


takes place. Now the only reason that the reverse reaction does not take place is that hydrogen chloride is a gas and is not soluble in the concentrated sulphuric acid. It therefore escapes from the sphere of action, and the reaction which results in its formation proceeds to completion.

It is also a general rule that *whenever any product of a possible reaction is volatile and can escape from the sphere of action, that reaction will take place.*

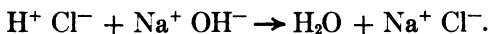
That the direction of the above reaction is dependent on the conditions which favor the escape of hydrogen chloride can be proved by observing the effect of altering the conditions. Hydrogen chloride we know to be extremely soluble in water; therefore if it is formed by a reaction carried out in a water solution, it will not escape from the sphere of action. When sulphuric acid is added to a *solution* of sodium chloride, no effect is noticed because the reaction comes to a standstill almost immediately. It may even be shown that

the reaction can be forced in the opposite direction when the reaction products are brought together in high concentration, for if hydrogen chloride gas is passed into a nearly saturated solution of sodium sulphate, a heavy precipitate of sodium chloride is thrown down,



421. Formation of Undissociated Substances. We have already learned that the neutralization of an acid and a base consists in the formation of un-ionized water from the hydrogen ions of the acid and the hydroxyl ions of the base. It is a general rule that *whenever different ionized substances are brought together in solution, if any possible new combination of ions can yield a substance whose ability to ionize is small, that substance will form.*

The neutralization of a strong acid with a strong base is a non-reversible reaction. For example, take the neutralization of hydrochloric acid by sodium hydroxide. Both of these substances exist mainly in the form of ions in dilute solutions. When they are mixed, the H^+ and OH^- ions unite completely in the formation of undissociated water:

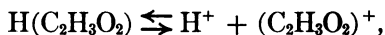


There is no tendency to make this reaction reverse, for the only possible undissociated compound on either side of the equation is water.

422. Neutralization of Weak Acids and Weak Bases. Acetic acid is a good example of a weak acid, since in a moderately dilute solution, it is only about one per cent ionized, that is to say, one in every one hundred molecules is separated into ions, $\text{H}(\text{C}_2\text{H}_3\text{O}_2) \rightleftharpoons \text{H}^+ + (\text{C}_2\text{H}_3\text{O}_2)^-$, whereas the other ninety-nine are intact. Ammonium hydroxide is a base of almost the same degree of ionization as acetic acid.

Both this acid and this base display a slight electrical conductivity, but only slight, for they cause the incandescent filament to glow just visibly when they are tested separately in the conductivity apparatus described on page 301. But if the acid and base solutions just tested for conductivity are poured together and the mixed solution is tested, it causes the incandescent filament to glow with its full brilliancy, thus showing a conductivity about equal to that of any fully ionized salt. By merely mixing two solutions of weak conductivity, we obtain one which conducts strongly.

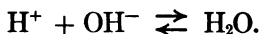
But this apparent magic is easily explained according to our knowledge of the equilibrium conditions of reversible reactions. In the acetic acid solution, the few ions are in equilibrium with the undissociated molecules according to the reversible reaction



and a like condition holds in the solution of ammonium hydroxide,



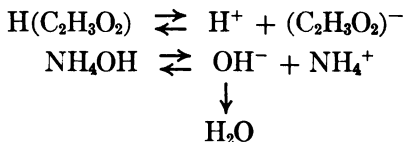
But when we mix the solutions, more H^+ and OH^- ions are brought together than can exist in equilibrium with water in the reversible reaction



Consequently, these ions disappear because they unite to form water. But this destroys the equilibrium which existed between the undissociated acid and its ions and between the undissociated base and its ions. The acid and base dissociate further to produce more H^+ and OH^- ions, respectively, in an attempt to reestablish equilibrium, but equilibrium cannot be established because the H^+ and OH^- ions are continuously

removed in the formation of water as fast as they are formed by the ionization of the acid and base.

If equivalent amounts of the weak acid and weak base are taken at the outset, they neutralize each other almost as completely as do strong acids and bases, but the reaction is more complicated. In addition to the formation of water from the H^+ and OH^- ions, the progressive ionization of the acid and base takes place. The negative ion of the acid and the positive ion of the base thus formed remain as ions in the solution — as the highly ionized salt — and it is these new ions that account for the very great increase in conductivity. The whole course of the reaction may perhaps best be shown by the following scheme :



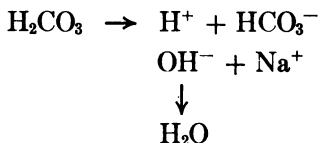
NEUTRALIZATION OF A WEAK ACID AND A WEAK BASE

The two reactions written horizontally are ordinarily reversible and by themselves tend far more strongly to run towards the left. When, however, certain of their products are almost completely withdrawn as fast as they are formed, as by the formation of water in the vertically written reaction, the horizontal reactions are able to run nearly to completion towards the right. The other products formed in the horizontal reactions accumulate in the solution and form the ionized and highly conducting salt, $\text{NH}_4^+ (\text{C}_2\text{H}_3\text{O}_2)^-$.

423. Incompleteness of the Neutralization of Very Weak Acids and Bases. When an acid or base is very weak, that is, much weaker than acetic acid or ammonium hydroxide, its neutralization is less complete but otherwise takes place in the same manner. It dissociates progressively as fast as its dissociation product, the H^+ or the OH^- ion, as the case may be,

is removed through the formation of water. Although water on the one side is the least dissociated of all the substances concerned in the reaction, yet the acid or base on the other side is very little dissociated. According to the rule above stated that reactions tend to run in the direction in which they will form un-ionized substances, we have two tendencies pulling in opposite directions. Water being the least dissociated, the whole reaction tends more strongly in the direction of neutralization.

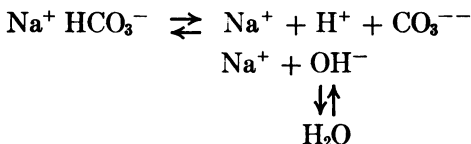
Carbonic acid is a very weak acid. As its formula shows, its molecules contain two acid hydrogens. One of these hydrogens is given off far more easily than the other, but the first one dissociates less easily than the hydrogen of acetic acid. About one tenth of one per cent of the molecules of H_2CO_3 ionize into H^+ and HCO_3^- ions. When treated with one mole of sodium hydroxide, carbonic acid reacts almost completely in the direction of the arrows in the diagrammatic scheme



REACTION OF CARBONIC ACID WITH ONE MOLE OF SODIUM HYDROXIDE

Neutralization is practically complete. Negative bicarbonate ions, HCO_3^- , accumulate and, balanced by Na^+ ions, form the ionized salt sodium bicarbonate, $\text{Na}^+ \text{HCO}_3^-$.

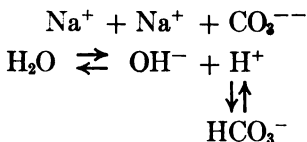
The ion HCO_3^- itself acts as an acid, $\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{--}$, although to a far less degree than the original H_2CO_3 ; and if a second mole of sodium hydroxide is added, the reaction represented in the following scheme takes place, although it does not progress to completion :



REVERSIBLE REACTION OF SODIUM BICARBONATE WITH
SODIUM HYDROXIDE

Neutralization is only partial with an acid so weak as HCO_3^- . To indicate this fact, the arrows are made to point in both directions.

424. Hydrolysis. Hydrolysis is the exact reverse of neutralization. When an acid and a base are brought together, neutralization takes place to a greater or less extent, water and a dissociated salt being formed; but when a pure salt is treated with water, hydrolysis takes place to some extent if either the acid or the base, or if both, are very weak.



HYDROLYSIS OF SODIUM CARBONATE

Water ionizes to a very small extent into H^+ and OH^- ions. The H^+ ions are continuously removed by the CO_3^{--} ions to form HCO_3^- and so the water is allowed to ionize continuously. The OH^- ions accumulate and impart the alkaline character to the solution. Before the hydrolysis has progressed far, it is brought to a standstill by the opposed reaction of neutralization, as indicated by the reversed arrows.

Thus, for example, if we bring together sodium carbonate and water, we observe hydrolysis, for the resulting solution is found to be alkaline to the taste and to turn red litmus blue. On the other hand, a salt of a strong acid and a strong base, for example sodium chloride, is neither alkaline nor acid. Sodium carbonate dissociates at once in water,

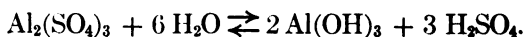
$\text{Na}_2\text{CO}_3 \rightarrow 2 \text{Na}^+ + \text{CO}_3^{--}$, but the CO_3^{--} ion cannot exist by the side of even the few H^+ ions coming from water without reacting to form HCO_3^- . Removal of even a part of the few ions which water normally yields allows water to ionize further, and since the new H^+ ions combine further with CO_3^{--} ions, the reaction of hydrolysis progresses in this manner until it is overcome by the opposing reaction of neutralization.

425. Alkalinity of Salts of Very Weak Acids. Many salts of weak acids and strong bases are of great service on account of their mildly alkaline reaction. Sodium carbonate is commonly known as washing soda and its usefulness in cleansing is determined by its mild alkalinity. Hydroxyl ions have the property of causing grease and dirt to emulsify, that is, to separate into innumerable little globules, so that they are readily floated off with water.

Soap is a sodium or potassium salt of the weak organic acids which are constituents of fats. Hydrolysis of soap plays an important part in the cleaning action, although it is true that soap is a much more effective cleaning agent than solutions of sodium hydroxide or of sodium carbonate of an equal degree of alkalinity.

Borax is the sodium salt of the weak boric acid, and borax is often used to give a mildly alkaline reaction.

426. Acidity of Salts of Very Weak Bases. Salts of very weak bases and strong acids show *acid* characteristics when dissolved in water. For example, aluminium sulphate, $\text{Al}_2(\text{SO}_4)_3$, is the salt of the weak base $\text{Al}(\text{OH})_3$ and the strong acid H_2SO_4 . Its hydrolysis produces equivalent amounts of the weak and inactive base and the strong and active acid



Hence the solution turns blue litmus red. Alum, which contains aluminium sulphate, is sometimes used in baking powder on account of its slightly acid character.

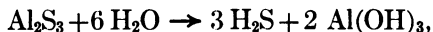
The hydroxides of the heavy metals are all very weak bases. Hence the salts are inclined to hydrolyze. Thus solutions of such salts as ferric chloride, FeCl_3 ; ferric sulphate, $\text{Fe}_2(\text{SO}_4)_3$; ferric nitrate, $\text{Fe}(\text{NO}_3)_3$; tin chloride, SnCl_2 ; mercuric nitrate, $\text{Hg}(\text{NO}_3)_2$, — all possess an acid character and are able to turn blue litmus red.

427. Extent of Hydrolysis. The hydrolysis of a salt always produces equivalent quantities of acid and base. Hydrolysis cannot occur at all if the acid and base are both moderately strong, but if one is weak, its weakness determines the degree of hydrolysis. Since the weak one is undissociated, it is itself inactive and the other imparts its acid or alkaline character to the whole solution.

If the acid and base are both very weak, the hydrolysis is all the more complete. For example, aluminium sulphide is the salt of the weak base $\text{Al}(\text{OH})_3$, and the weak acid H_2S . It can be made in the dry way by heating together aluminium and sulphur,

$$2 \text{ Al} + 3 \text{ S} \rightarrow \text{Al}_2\text{S}_3.$$

When it is treated with water, hydrolysis takes place,



with a vigorous effervescence due to the escape of hydrogen sulphide and the formation of a flocculent insoluble residue of aluminium hydroxide. Hydrolysis is complete in this case, but no marked alkaline or acid effect is noted because both the acid and the base are very weak.

The useful hydrolyzable salts are all composed of either a weak acid and a strong base or of a strong acid and a weak base. The extent of the hydrolysis is rarely larger than a

few per cent of the salt, although it varies, of course, according to the weakness of the acid or base. For example, a solution of sodium carbonate is of about the same degree of alkalinity as a solution of ammonium hydroxide of equivalent concentration, and we have already found that ammonium hydroxide is only about one per cent ionized.

428. Uses of Hydrolyzable Salts. When it is desired to produce for practical purposes a solution of mild alkalinity or acidity, the use of hydrolyzable salts has very great advantages over the use of very small amounts of strong bases or acids. For example, suppose the housewife were to use sodium hydroxide to scrub the kitchen floor. Knowing little of chemistry, she might take too much, and the skin would be taken from her hands and the floor surface would be injured. Washing soda gives only a very small per cent of sodium hydroxide, and she cannot take enough to give more than the desirable mild alkalinity.

Suppose, however, that she was careful to take just the small amount of sodium hydroxide necessary to give the proper alkalinity. A little acid on the floor, as for example from crushed fruit or spilled vinegar, would quickly neutralize the small amount of base and destroy the alkalinity. On the other hand, if she used washing soda, the acid would be neutralized, but more of the salt would at once hydrolyze to maintain the alkalinity.

A similar condition governs the use of acid substances in baking powder. Sulphuric acid would be out of the question, but alum, which hydrolyzes to give a little sulphuric acid, is useful. As fast as the sulphuric acid so formed is used up in reacting with the sodium bicarbonate of the baking powder, the alum hydrolyzes further until finally it has yielded its entire store of sulphuric acid.

Another important use of a hydrolyzable salt is in the settling of muddy water for municipal use. Sedimentation alone would be too slow a process, although it would help greatly. Aluminium sulphate is therefore added to the muddy water, whereupon hydrolysis results, yielding a precipitate of gelatinous aluminium hydroxide and sulphuric acid. The gelatinous aluminium hydroxide in settling carries down most of the suspended material with it, leaving clear water. The sulphuric acid which also results reacts with calcium bicarbonate (present in most water supplies) and forms calcium sulphate, which is harmless, and carbonic acid, which decomposes into water and carbon dioxide.

429. Importance in Living Organisms. The delicate regulation of acid or alkaline qualities that is possible with hydrolyzable salts is not only made use of practically in the household and in the chemical factory, but it occurs extensively in nature. It is essential to the life processes that the blood of men and animals and the juices of plants be maintained at the exact degree of alkalinity or acidity required by the organism, and the regulation is usually effected by the presence of hydrolyzable salts. The human blood is maintained at almost the exact neutral point by means of a mixture of several hydrolyzable salts, important among which is sodium phosphate. If the blood varies appreciably to either side of this point, death will almost immediately ensue. These salts constitute a reservoir of neutrality. Suppose they were not present and that a person took lemon juice (citric acid) into his stomach. This would pass into the blood and rapidly increase its acidity and cause death. But with sodium phosphate present, the citric acid is neutralized by the base progressively set free by hydrolysis. If considerable alkali is taken into the stomach, the blood does

not become alkaline, but its neutrality is maintained by a similar process.

430. In the following tables, some of the important hydrolyzable salts are summarized :

SALT	FORMULA OF SALT	WEAK ACID	STRONG BASE	REACTION OF SALT SOLUTION
Washing Soda	Na_2CO_3	HCO_3^-	NaOH	Distinctly alkaline
Baking Soda	NaHCO_3	H_2CO_3	NaOH	Barely alkaline
Borax	$\text{Na}_2\text{B}_4\text{O}_7$	$\text{H}_2\text{B}_4\text{O}_7$	NaOH	Mildly alkaline
Soap	$\text{Na}(\text{C}_{18}\text{H}_{35}\text{O}_2)^1$	$\text{H}(\text{C}_{18}\text{H}_{35}\text{O}_2)$	NaOH	Mildly alkaline
Sodium Phosphate	Na_3PO_4	HPO_4^{--}	NaOH	Strongly alkaline
	Na_2HPO_4	H_2PO_4^-	NaOH	Mildly alkaline
	NaH_2PO_4	$\text{H}(\text{H}_2\text{PO}_4)$	NaOH^2	Mildly acid

SALT	FORMULA OF SALT	STRONG ACID	WEAK BASE	REACTION OF SALT SOLUTION
Alum	$\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$	H_2SO_4	$\text{Al}(\text{OH})_3$	Mildly acid
Aluminium sulphate	$\text{Al}_2(\text{SO}_4)_3$	H_2SO_4	$\text{Al}(\text{OH})_3$	Mildly acid
Sal Ammoniac	NH_4Cl	HCl	NH_4OH	Neutral to litmus
Ferric Chloride	FeCl_3	HCl	$\text{Fe}(\text{OH})_3$	Acid
Gold Chloride	AuCl_3	HCl	$\text{Au}(\text{OH})_3$	Strongly acid

SUMMARY

Many chemical reactions are practically complete under ordinary conditions, that is, they proceed entirely in one direction until either one (or all) of the reacting substances is used up.

Chemical affinity is the force which causes substances to combine.

This force cannot be altered by changing exterior conditions,

¹ This is the formula of sodium stearate, which is one of the many similar salts which constitute soaps.

² Insufficient to neutralize acid.

but the exterior conditions may produce forces which can overcome this chemical affinity. Thus reactions can often be made to run in the opposite direction by the application of intense heat or of an electric current.

Effect of Mass. A number of reactions are capable of reversal even under ordinary conditions. Such reactions are governed largely by the mass of the reacting substances. Increase in the mass of the reacting materials causes the reaction to proceed farther. Increase in the mass of the products of the reaction causes the change to proceed in the reverse direction.

Chemical Equilibrium. A reversible reaction seeks to reach a state of chemical equilibrium which is a condition of apparent rest. The substances on one side of the reaction equation exist in the presence of the substances on the other side. Although at the point of equilibrium there is no apparent change taking place, still it is believed that both of the opposed reactions are taking place, — only with equal velocities so that the total of the resulting change is zero.

Removal of Products of Reaction. If a substance involved in a reversible reaction is continually removed so that the reaction cannot reach a condition of equilibrium, the reaction may thus be made complete in this direction.

Substances may be removed from the sphere of action by precipitation or by volatilization. Un-ionized substances are practically inactive so that when they are formed the effect is as if they were withdrawn from the sphere of action. Hence the general rule: Whenever a reaction in solution is possible which can produce a precipitate, a volatile product, or an undissociated substance, that reaction will take place.

Neutralization and Hydrolysis. Neutralization is a reaction in which the undissociated substance, water, is formed. Hydrolysis is the exact reverse of neutralization. Hydrolysis can take place by the action of water with the salt of a very weak acid or a very weak base.

Some of the hydrolyzable salts are of very great usefulness on account of the mild degree of alkalinity or acidity of their solutions.

Questions

1. Give several reactions that you have already studied which are capable of being reversed.
2. Tell of one means by which reactions are made to reverse themselves.
3. What is meant by the term *equilibrium*?
4. Give three methods of causing a reaction that is reversible in its nature to proceed to completion in one direction.
5. What is meant by hydrolysis?
6. Why does sodium carbonate, which is salt, have an alkaline reaction in water solution?
7. Name three substances the principal uses of which depend upon their ability to hydrolyze.
8. Apply the idea of equilibrium to the reversible reaction $\text{NaCl} \rightleftharpoons \text{Na}^+ + \text{Cl}^-$, in a solution of common salt. How would this equilibrium be affected (a) by adding a solution of silver nitrate, (b) by evaporating off the water?
9. Does guncotton exist in a state of chemical equilibrium? What would you do to make guncotton come to a state of equilibrium? What is the reaction and is it a reversible one?

CHAPTER XXXIII

CHEMICAL REACTIONS AND ENERGY TRANSFORMATIONS

IN the first chapter of this book it was stated that one of the most noticeable characteristics of chemical changes is the evolution of heat and often of light. Not all changes, it is true, develop as much heat as the oxidation of charcoal; in fact, some reactions absorb heat; it is, however, true without exception that all reactions are accompanied by some kind of an energy change.

431. Different Forms of Energy. Energy manifests itself in many forms, of which heat is only one. The heat produced by a coal fire can be made to run a steam engine in which a part of the heat is transformed into mechanical energy. This in turn can be made to rotate the coils of a dynamo and produce electric energy. The later can be turned back again into mechanical energy by means of an electric motor, or it may be converted into heat in an electric stove, or into heat and light in an incandescent lamp, or into chemical energy by being made to decompose some chemical compound.

432. Chemical Energy. When an electric current is forced to pass through acidulated water, the latter is decomposed into hydrogen and oxygen. The energy possessed by these two elements is thereby increased by an amount equal to the electric energy expended in decomposing the water.

It is true that hydrogen and oxygen remain quiescent at ordinary temperature for an indefinitely long time. This

energy may be compared to the energy of water in a reservoir in a high mountain valley. The water is quiescent so long as it remains in the reservoir; but if the gate is opened which allows it to flow downhill to a water wheel, its stored-up energy can do mechanical work. In a similar way, hydrogen and oxygen when uncombined possess stored-up energy which may be set free by starting them in reaction with a tiny flame or a spark. If a mixture of the two is exploded, the expansion can be made to do mechanical work, or if the gases are slowly fed to each other and burned, the heat of their union can be used in heating a steam boiler.

433. Exothermic Reactions. A reaction which, like the combination of oxygen and hydrogen, gives off heat as it proceeds, is known as an exothermic reaction (meaning to give off heat). In general, all reactions which proceed of themselves when once started are exothermic, and the amount of heat or other form of energy given off is a measure of the tendency which the reaction had to take place.

It is fortunate that strongly exothermic reactions such as the burning of coal and wood do not commence spontaneously. The energy stored up in wood and coal, except for slow decay, which can be likened to the leakage of energy, stays stored up waiting for the hand of man to call it into useful action by the application of the kindling flame.

Most chemical reactions that are carried out in the laboratory are exothermic, although many yield so little heat or yield it so slowly under the conditions of the experiment that its escape is scarcely noticeable. For example, when substances in solution enter into reaction, the heat produced cannot be expected to produce incandescence; the water may be warmed in some cases so that it boils vigorously, but more often it will be warmed only a few degrees.

When pure, dry substances react and the heat of the reaction all goes to warming a limited amount of solid or molten material, the temperature may rise very greatly. Thus a mixture of zinc filings and powdered sulphur rises to incandescence when a reaction is started.

434. Aluminothermy. A very high temperature can be obtained by the reaction of granulated aluminium with iron oxide:



The mixture of iron oxide and aluminium is placed in a refractory crucible and a little fuse powder is placed on top. The fuse powder when ignited produces an intense local heat and this starts the reaction of the main mixture. A reference to the potential series of the metals (page 329) shows that aluminium stands high in the series and therefore that it must be a very active metal.



FIG. 74.—Preparing Molds about Rail Joints for welding with Thermit.

It takes oxygen away from the iron oxide, and the heat of formation of the aluminium oxide so far exceeds the heat necessary to decompose the iron oxide that a large excess is left to heat the residual iron and the aluminium oxide. This heat is all confined within the crucible, for no gaseous products are formed to carry away part of it. The iron and aluminium oxide are thus not only melted, but are raised

to a temperature — about 3000°C . — approaching that of the electric arc.

This process represents the highest temperature which can be obtained for industrial purposes by means of a chemical



FIG. 75. — Crucibles containing Thermit in Place over Molds. The rubber hose shown delivers a blast for the preheating process.

reaction. A mixture of iron oxide and aluminium is a commercial product and is sold under the name of Thermit. One of the important applications of Thermit is in the welding together of iron and steel parts as, for example, the parts of a broken propeller shaft of a steam vessel and the

rails of the car track. The crucible is so arranged that the molten iron which sinks to the bottom can be tapped off and run into a mold placed around the joint to be welded. The iron is so hot that it melts the surfaces of the broken ends, which thus become welded to a perfectly solid joint. In making welds in large pieces, it is a common practice to preheat the pieces to be welded with a blast flame. This prevents conduction and loss of so much of the heat contained in the welding steel which comes from the crucibles and so insures a more perfect weld.

435. Familiar Exothermic Processes. The most extensive industrial chemical reaction is the combustion of fuel for the production of heat, light, and power, and in this case

the energy set free is all that is sought from the reaction; the material products are of no value, and the residues, such as ashes and smoke, are a source of annoyance and expense.

Most of the chemical reactions in which it is the material products that are sought are also of the exothermic type. For example, in the manufacture of sulphuric acid, the oxidation of the sulphur yields heat at both stages (Chapter XXIX) and the union of sulphur trioxide with water also yields heat.

The reactions that take place in animal bodies are also exothermic and serve to warm and move the body, while the material products of the reaction are waste and have to be eliminated. The food, which is the fuel with which the body is fed, is not all burned at once, but a large part of it is slightly altered chemically without much loss of energy and stored up as muscular tissue and fat. In this form it remains temporarily, but finally it suffers combustion like the rest of the material assimilated by the body.

436. Exothermic and Endothermic Compounds. If heat or other form of energy is evolved by the reaction in which a compound is formed by the combination of its constituents, the compound is said to be exothermic. Exothermic compounds, such as water, zinc sulphide, aluminium oxide, are stable, that is to say, they never decompose of themselves and can only be decomposed by the expenditure of energy in some form, — such as electrical or chemical.

When heat or other form of energy is absorbed in the formation of a compound from its constituents, that compound is said to be endothermic (meaning heat is absorbed). Nitroglycerine is an example of an endothermic compound. In general, such compounds are not stable and they tend to decompose, thereby giving off energy; in fact many of them

decompose explosively when the reaction gathers sufficient headway. The energy given off when nitro-glycerine decomposes is used in blasting, — the blasting material dynamite is infusorial earth or other porous substance impregnated with nitroglycerine.

437. Photosynthesis. We see on every hand examples of exothermic chemical change, the burning of fuels, the decay of wood, the consumption of foods, and the majority of the thousands of chemical reactions employed in the manufacturing industries. In all of these changes, chemical energy is converted into heat. The thought naturally arises, will not all of the chemical energy become exhausted, or, in other words, will not all of the materials which can react exothermically become used up? It will be recalled, however, from the chapters on carbon and particularly from the section on the carbon cycle in nature, that all fuels and foods contain carbon as one of their chief constituents. The carbon dioxide formed by the combustion of these materials does not remain long in the atmosphere, but reacts with water in the green leaves of plants, whereby sugars are built up and oxygen is released again to the atmosphere. The sugar so formed may be changed in the plant into starch, cellulose, or other sugars, and ultimately the wood may be converted into coal, so the sugar formed in the green leaves is the parent substance of all foods and fuels. The combustion of sugar, or any food or fuel, to form carbon dioxide and water is a strongly exothermic reaction. Consequently, carbon dioxide and water cannot of themselves, — nor even with the aid of catalyzers, — react to form sugar and oxygen. Energy must be applied to compel this change, and this energy is supplied by sunlight. The chlorophyll of the green leaves does not cause this chemical change, but its function is to direct the action of the light

energy, just as the function of a harness is to make the power of a horse available, or the function of a water wheel and dynamo is to convert the energy of falling water into usable electric energy.

Thus the energy of the sun is the great source of the chemical energy stored up in foods and fuels. The building up process is called photosynthesis, meaning the putting together through the agency of light.

438. Energy Changes and the Carbon Cycle. From what has just been said, it is seen that not all of the sun's energy goes at once to simply warm the surface of the earth. Some of it first traverses a circular path, entering, so to speak, into single revolutions of the carbon cycle. On the one side of the cycle, the green plants, by using water and carbon dioxide as materials, and sunlight as energy, are storing up chemical energy by means of endothermic reactions. On the other side, man is supplying his needs, both external and internal, and all animals, and also bacteria and fungous plants, which live upon other plants or upon animal tissues, — all these are bringing about exothermic reactions by which chemical energy is released, ultimately becoming heat, and the simpler substances, water and carbon dioxide, are once more formed as a result of the combustion or decay that takes place.

The material elements of the cycle are ready to go through another revolution, but the energy necessary to carry on the cycle must again be obtained from the sunlight. The form in which energy is given off at the end of each cycle cannot be again utilized by the green plants.

It is a law of physical science that no energy can be lost, and this is as fundamental as is the law that matter cannot be destroyed. All forms of energy tend, however, to change into heat. Heat energy, where there are differences in tem-

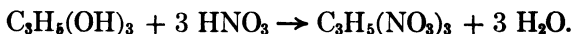
perature (intensity), can be partly converted into other forms, as for example by the steam engine, but uniformly distributed heat cannot be converted into useful forms of energy. Thus large bodies of water contain enormous quantities of uniformly distributed heat, but this form of energy cannot be made to propel vessels. The earth is all the time losing energy by the radiation of heat into space, and this loss is probably a trifle greater than the gain from the energy received from the sun.

439. Artificial Preparation of Endothermic Substances.

As already stated, reactions naturally tend to proceed in the direction in which energy is evolved, and outside of photosynthesis, comparatively few endothermic processes are observed in nature. Yet it is possible by bringing forces into play in the right manner to cause artificially the formation of endothermic substances, and man's ingenuity has devised many ways in which to manufacture useful compounds of this type.

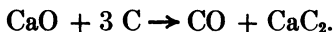
Nitric oxide, NO, is strongly endothermic. When it is made from atmospheric oxygen and nitrogen by the electrical method (page 71), its energy is derived from the heat of the electric spark. Nitric oxide is of importance mainly from the fact that nitric acid can be made from it. Nitric oxide combines with oxygen and water by an exothermic process — one which therefore takes place without further application of energy — to form nitric acid.

Nitroglycerin. From nitric acid are derived practically all of the explosive substances in commercial use. Typical of these explosives is nitroglycerin, which is made from nitric acid and glycerol, according to the following reaction :



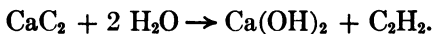
One of the products of this reaction is the highly exothermic substance water, and the energy liberated by its formation is in large part added to the energy already possessed by the nitric acid and the glycerol in building up the energy content of the nitroglycerin. Furthermore, concentrated sulphuric acid must be added to the reaction mixture (see manufacture of guncotton, page 370) in order to carry forward the reaction. Water and sulphuric acid mix with the evolution of heat, and, although we do not write any definite chemical equation for this combination, still it is obviously a strong exothermic process. Its energy is likewise available for the building up of the energy of the nitroglycerin.

Calcium carbide is an endothermic compound, and it is formed in the electric furnace according to the reaction :



The formation of carbon monoxide is exothermic, and the energy thus liberated, as well as that of the intense heat of the furnace, is available to add to the energy already possessed by the calcium and carbon.

Acetylene is made by the action of water on calcium carbide :



Calcium hydroxide is an exothermic substance and its formation aids in the formation of the highly endothermic acetylene. Acetylene is so highly endothermic that it is dangerously explosive even when unmixed with air. It can ordinarily be handled and burned with a fair degree of safety ; but when once its decomposition is violently started, it continues with great violence. The great amount of heat liberated by its decomposition causes a sudden and violent expansion and it is

this that does the damage. One reads occasionally of serious explosions occurring in acetylene factories.

The endothermic character of acetylene adds to its value as a fuel, for not only is the heat of formation of carbon dioxide and water yielded by its combustion, but added to this is its own very considerable heat of decomposition. The acetylene flame is, therefore, much hotter than the ordinary gas flame and on that account, as well as because it contains more luminous carbon particles (see page 275), it is far more luminous. The oxyacetylene flame is much used in place of the oxyhydrogen flame (see page 116) on account of the superior degree of heat it produces.

Ozone is a more active form of oxygen because it is possessed of a higher energy content. In the reaction by which it is formed from ordinary oxygen, $3 \text{O}_2 \rightarrow 2 \text{O}_3$, energy is absorbed from the electric impulses which constitute the so-called silent electrical discharge.

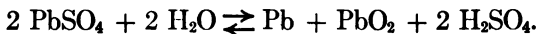
The formation of **hydrogen peroxide** from water and oxygen involves the acquisition of energy and it is this energy which accounts for the activity of hydrogen peroxide. Dilute solutions of hydrogen peroxide are not dangerous but the pure substance is highly explosive.

440. Theory of Explosions. Whether an explosion takes place from the union of two substances, as, for example, hydrogen and oxygen, or from the decomposition of a substance like nitroglycerin or acetylene, the theory is the same. The explosive reaction is an exothermic one. So long as the temperature is low and no shock is given, the reaction does not acquire any headway; but when it once commences to a considerable extent, its own progress furnishes heat which raises the temperature. The rise in temperature promotes the speed of the reaction itself; thus more heat is furnished and

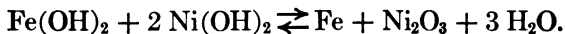
so on, and in an inconceivably short space of time the reaction is finished.

Some substances explode more easily than others; nitroglycerin goes off with extreme ease and is one of the most dangerous explosives to handle. Guncotton is far safer, and, in fact, it can usually be burned in the open air without exploding. Yet, when it is exploded by detonation, its power is not much inferior to that of nitroglycerin. Acetylene can be burned with safety as an illuminant, yet when it is detonated, it is an explosive of a good deal of power.

441. The Storage Battery is an arrangement of electrochemical cells in which electrical energy can be converted into chemical energy by causing an endothermic reaction to take place. When charged, the battery is ready to give back all the energy it received. The chemical reaction takes place in the reverse direction, and in so doing it causes an amount of electricity, equal in amount and opposite in direction to the charging current, to flow. The reversible reaction which takes place in the usual type of lead storage battery is



The reversible reaction in the Edison storage battery is substantially as follows:



SUMMARY

Exothermic reactions are accompanied by an evolution of energy so that the energy content of the product, or products, is less than that of the reacting substances. The energy released is most commonly in the form of heat, but it may be in some other form, as, for example, electrical energy or light. Most reactions that take place in nature and the majority of those that are carried out in the laboratory and in manufacturing processes are of the exothermic type.

Endothermic reactions are those in which the energy content of the products is greater than that of the reacting substances. Very important endothermic reactions take place in the green leaves of plants and some of the energy of sunlight is thereby converted into stored-up chemical energy. The material products which are stored up in the plants are carbohydrates, and the process is called photosynthesis.

The chemical energy continually being stored up by plants in forming carbohydrates and oxygen from carbon dioxide and water is continually being used up in satisfying the wants of men and animals, and in very large amount being wasted by decay and useless fires.

Exothermic compounds are stable, whereas endothermic compounds are unstable and many of them are explosive.

Endothermic compounds are made artificially, sometimes by utilizing electric energy, sometimes heat energy, and sometimes the energy liberated in the formation of exothermic compounds.

Questions

1. Cite several exothermic reactions which are carried out solely for the heat produced and in which the material products are merely waste.
2. Cite exothermic processes which yield energy as an electric current.
3. How do chemical processes store up the sun's energy?
4. Name several explosives in which the power is developed by the decomposition of an endothermic substance.
5. Describe explosive mixtures in which the power is developed through the formation of an exothermic compound.
6. To which of the sciences does the study of energy naturally belong? Why is it impossible to study any one science, such as chemistry, without overlapping into the other sciences?
7. Why is a knowledge of chemistry fundamental in the understanding of the sciences of physiology and geology?

APPENDIX

I. PRESSURE OF SATURATED WATER VAPOR

Temperatures in degrees centigrade. Pressures in millimeters of mercury

TEMP.	PRESS.	TEMP.	PRESS.	TEMP.	PRESS.
0	4.6	11	9.8	22	19.7
1	4.9	12	10.5	23	20.9
2	5.3	13	11.2	24	22.2
3	5.7	14	11.9	25	23.6
4	6.1	15	12.7	26	25.0
5	6.5	16	13.5	27	26.5
6	7.0	17	14.4	28	28.1
7	7.5	18	15.4	29	29.8
8	8.0	19	16.4	30	31.6
9	8.6	20	17.4	50	92.0
10	9.2	21	18.5	100	760.0

II. CORRECTION OF GAS VOLUMES FOR AQUEOUS VAPOR

When a gas is saturated with water vapor, the volume which it would occupy dry may be calculated with the aid of the above table and the following two rules.

In a mixture of two or more gases each gas exerts its own pressure independently of all the other gases present, and the total pressure is equal to the sum of the pressures which each one would exert if it were the only gas filling the space.

The amount of water which is able to evaporate into a definite space depends solely on the temperature and is independent of the quantity and kind of other gas which already fills the space.

If a little water is admitted to an evacuated vessel and the temperature is 20°C. , the water evaporates until the pressure of its vapor is 17.4 mm. (see foregoing table). If the vessel is already filled with dry air at 760 mm. before the water is admitted, — or forced in, — the water evaporates just the same until its pressure has reached 17.4 mm. A barometer placed in the vessel would now show a pressure of $760 + 17.4$ mm., provided the vessel were kept closed and its pressure were not allowed to equalize itself with that of the outside atmosphere.

Suppose we were measuring the volume of a gas by confining it over water at 20°C. and 760 mm. The gas is saturated with water vapor, the pressure of which at 20°C. is 17.4 mm. Since the total pressure is only 760 mm. and the gas itself is only one of the two gases which constitute the mixture, the pressure of the gas itself can be but $760 - 17.4 = 742.6$ mm.

In the problem on page 87 it was found that 45 c.c. of *dry* gas at 20°C. and 740 mm. would have a volume of 40.8 c.c. under standard conditions. Let us now calculate what would be its volume under standard conditions, if the gas had been saturated with water vapor when its volume was measured:

$$\text{pressure of gas} + \text{pressure of water vapor} = 740 \text{ mm.}$$

$$\begin{aligned}\text{pressure of gas} &= 740 - \text{pressure of water vapor} \\ &= 740 - 17.4 = 722.6 \text{ mm.}\end{aligned}$$

$$\begin{aligned}\text{vol. (standard)} &= \text{vol. (meas.)} \times \frac{\text{stand. temp.}}{\text{temp. of gas}} \times \frac{\text{press. of gas}}{\text{stand. press.}} \\ &= 45 \times \frac{273}{293} \times \frac{722.6}{760} \\ &= 39.9 \text{ c.c.}\end{aligned}$$

This volume is 0.9 c.c. less than the volume calculated for the dry gas, and we thus see that at 20° C. saturating a gas with water vapor increases its volume by 2 per cent when the total pressure is not allowed to increase.

Therefore in making accurate measurements the presence of water vapor should not be neglected when calculating gas volumes to standard conditions.

On the other hand, when a number of gas volumes are being measured over water all at about room temperature and it is necessary only to make a comparison of the different volumes, it is unnecessary to take the water vapor into account, because it is present in every case in almost the same proportion.

In correcting to the same conditions the volumes measured in determining the volume per cent of oxygen in air (page 85) the presence of water vapor was neglected. The pupil is advised to recalculate this problem, correcting all volumes to standard conditions (dry) and convince himself that the same per cent by volume of oxygen is found.

III. SOME PROPERTIES OF COMMON ELEMENTS

ELEMENT	SPECIFIC GRAVITY	MELTING POINT	BOILING POINT
Aluminium	2.7	657° C.	—
Calcium	1.58	800	—
Copper	8.9	1045	—
Gold	19.3	1065	—
Hydrogen	—	- 257	- 253° C.
Iron	7.8	1550	—
Lead	11.4	327	—
Mercury	13.6	- 39.4	357
Platinum	21.5	1770	—
Potassium	.87	62.5	720
Silver	10.5	955	—

III. SOME PROPERTIES OF COMMON ELEMENTS— *Continued.*

ELEMENT	SPECIFIC GRAVITY	MELTING POINT	BOILING POINT
Sodium	.97	95.6	742
Tin	7.3	233	—
Tungsten	19.1	above 3000	—
Zinc	7.2	420	918
Bromine	3.2 (liquid)	7	59
Carbon { diamond graphite amorphous	3.51	} 3500?	—
	2.25		
	1.70		
Chlorine	—	— 102	— 33.5
Nitrogen	—	— 214	— 196
Oxygen	—	— 227	— 181
Phosphorus (yellow)	1.82	44.2	269
Iodine	4.95	114	184
Sulphur { (rhombic) (monoclinic)	2.06	114.5	} 449
	1.96	119	

IV. WEIGHT OF ONE LITER OF VARIOUS GASES UNDER STANDARD CONDITIONS

GAS	FORMULA	WEIGHT
Air	—	1.29 grams
Ammonia	NH ₃	0.76
Argon	A	1.79
Carbon dioxide	CO ₂	1.98
Carbon monoxide	CO	1.25
Chlorine	Cl ₂	3.18
Fluorine	F ₂	1.70
Helium	He	0.18
Hydrogen	H ₂	0.09—
Hydrogen chloride	HCl	1.61
Hydrogen sulphide	H ₂ S	1.54
Methane	CH ₄	0.72
Nitrogen	N ₂	1.25
Nitric oxide	NO	1.34
Oxygen	O ₂	1.43 —
Steam (hypothetical)	H ₂ O	0.81
Sulphur dioxide	SO ₂	2.86

V. SOME PROPERTIES OF COMPOUNDS

NAME	FORMULA	SPECIFIC GRAVITY	STATE	MELTING POINT	BOILING POINT
Acetic acid (glacial)	$H(C_2H_3O_2)$	1.055	liquid above 17.5° C.	17.5° C.	119.0° C.
Acetone	C_3H_6O	0.79	liquid	—	56.3
Alcohol (grain)	C_2H_5OH	0.79	liquid	-130	78.4
Alcohol (grain) 95% constant boiling mixture	C_2H_5OH Aq	0.80	liquid	—	78.15
Alcohol (wood)	CH_3OH	0.79	liquid	-97.8	66
Ammonia	NH_3	$\left\{ \begin{array}{l} 8.5 (H_2 = 1) \\ 0.73 (H_2O = 1) \end{array} \right\}$	$\left\{ \begin{array}{l} \text{gaseous} \\ \text{liquid} \end{array} \right\}$	-75.5	-33.5
Ammonium hydroxide (28% NH_3)	$\left\{ \begin{array}{l} NH_4OH \\ NH_3 \text{ in solution} \end{array} \right\}$	0.90	solution	—	—
Carbon dioxide	CO_2	$\left\{ \begin{array}{l} 22.0 \\ 0.72 \end{array} \right\}$	$\left\{ \begin{array}{l} \text{gaseous} \\ \text{liquid} \end{array} \right\}$	—	-79
Carbon tetrachloride	CCl_4	1.59	liquid	—	77
Chloroform	$CHCl_3$	1.52	liquid	-63.2	61.2
Ether	$(C_2H_5)_2O$	.73	volatile liquid	-117	35
Hydrochloric acid (concentrated; 40% HCl)	HCl Aq	1.20	solution	—	—
Hydrochloric acid (constant boiling point mixture; 20.2% HCl)	HCl Aq	1.10	solution	—	110
Hydrogen chloride	HCl	$\left\{ \begin{array}{l} 18.2 \\ 0.8 \end{array} \right\}$	$\left\{ \begin{array}{l} \text{gaseous} \\ \text{liquid} \end{array} \right\}$	-116	-80
Hydrogen peroxide	H_2O_2	1.45	liquid	—	—
Hydrogen sulphide	H_2S	$\left\{ \begin{array}{l} 17.0 \\ .86 \end{array} \right\}$	$\left\{ \begin{array}{l} \text{gaseous} \\ \text{liquid} \end{array} \right\}$	-82.9	-61.8
Nitric acid (pure)	HNO_3	1.52	liquid	-47	86
Nitric acid (constant boiling point mixture (68% HNO_3))	HNO_3 Aq	1.42	solution	—	120.5
Petroleum products	Various hydrocarbons,				
(a) Petroleum ether	chiefly of the marsh gas series. The mean molecular weight increases with increase in the boiling point.	0.635 to 0.660	mixed liquid	—	40 to 70
(b) Gasoline		0.660 to 0.667	mixed liquid	—	70 to 80
(c) Benzine		0.667 to 0.707	mixed liquid	—	80 to 100
(d) Kerosene					
Grade I		0.753 to 0.864	mixed liquid	—	150 to 200
Grade II					200 to 250
Grade III					250 to 300
Phosphoric acid (ortho)	H_3PO_4	1.88	solid below 40.5° C.	40.5	—
Sulphur dioxide	SO_2	$\left\{ \begin{array}{l} 32 \\ 1.43 \end{array} \right\}$	$\left\{ \begin{array}{l} \text{gaseous} \\ \text{liquid} \end{array} \right\}$	-76.1	-8
Sulphuric acid (98% H_2SO_4)	$H_2SO_4 \cdot \frac{1}{2} H_2O$	1.84	liquid	below 0	383
Sulphuric acid (monohydrate)	$H_2SO_4 \cdot H_2O$	1.79	liquid	8	—
Sulphur trioxide	SO_3	$\left\{ \begin{array}{l} 1.90 \\ 1.97 \end{array} \right\}$	$\left\{ \begin{array}{l} \text{liquid} \\ \text{solid} \end{array} \right\}$	14.8	46 50

VI. SOLUBILITIES OF SOME BASES AND SALTS

Grams of Substance Soluble in 100 cc. of Water at 18° C.

	K	Na	Ag	Ba	Ca	Mg	Zn	Pb
Cl	33	36	0.0,16	37	73	56	204	1.5
Br	66	89	0.0,1	104	143	103	478	0.60
I	137	178	0.0,3	201	200	148	419	0.08
NO ₃	30	84	213	8.7	122	74	118	52
ClO ₃	6.6	97	12	35	179	126	184	151
SO ₄	11	36	0.55	0.0,23	0.20	35	53	0.004
CO ₃	108	19	0.003	0.0023	0.0013	0.1	0.004 ?	0.0,1
OH	149	116	0.01	3.7	0.17	0.001	0.0,5	0.01

VII. GENERAL RULES OF SOLUBILITY

In addition to the above exact figures for the solubility of a few substances, the following approximate rules are of value :

1. All salts of the *alkali metals* (Na, K, NH₄) are soluble.
2. All *bromides* are soluble except those of Ag, Hg, Pb.
3. All *carbonates* are insoluble except those of the alkali metals.
4. All *chlorates* are soluble.
5. All *chlorides* are soluble except those of Ag, Pb, and Hg(ous).
6. All *hydroxides* are insoluble except those of the alkali metals (Na, K, NH₄), Ba, and Sr.
7. All *nitrates* are soluble.
8. The *oxides* of the heavy metals are insoluble and do not react with water. The oxides of the alkali metals, Ca, and Ba react vigorously with water to form the hydroxides.
9. All *phosphates* are insoluble except those of the alkali metals.
10. All *silicates* are insoluble except those of the alkali metals. Glass and rocks, such as feldspar and mica, are insoluble, although they contain silicates of the alkali metals mixed with other silicates.
11. All *sulphates* are soluble except those of Ba, Ca, Sr, and Pb.

VIII. IMPORTANT TEMPERATURES

1. Zero absolute	- 273° C.	22. Dull red heat	650
2. Boiling point of helium	- 268.5	23. Melting point of alumin- ium	660
3. Melting point of hydrogen	- 260	24. Melting point of com- mon salt	792
4. Boiling point of hydrogen	- 252.6	25. Red heat	800
5. Melting point of nitrogen	- 214	26. Bright red heat	1000
6. Boiling point of nitrogen	- 194	27. Melting point of gold	1064
7. Boiling point of oxygen	- 182.5	28. Melting point of copper	1090
8. Freezing point of grain al- cohol	- 130	29. Yellow heat	1200
9. Freezing point of mercury	- 39.5	30. White heat	1350
10. Freezing point of water	0	31. Temperature of glass furnace	1375
11. Average room tempera- ture	20	32. Melting point of iron	1520
12. Normal temperature of the body	37	33. Melting point of plat- inum	1750
13. Melting point of Wood's metal	60	34. Melting point of corun- dum	2000 ±
14. Boiling point of grain al- cohol	78.5	35. Melting point of irid- ium	2300
15. Boiling point of water	100	36. Temperature of oxyhy- drogen flame	2500 ±
16. Melting point of rhombic sulphur	114.5	37. Melting point of os- mium	2500
17. Melting point of tin	232	38. Temperature of oxy- acetylene flame	above 2700
18. Melting point of lead	327	39. Melting point of tung- sten	3000
19. Melting point of zinc	419	40. Temperature of alu- mino-thermy	3500 ±
20. Boiling point of sulphur	445	41. Temperature of electric arc	4000 ±
21. Incipient red heat	550	42. Temperature of sun	6000

IX. COMPOSITION OF ALLOYS

TYPE OF ALLOY	NAME	APPROXIMATE COMPOSITION IN PARTS PER 100
Copper Alloys	Brass	Cu (67-80); Zn (20-33); Pb $\frac{1}{2}$ ±
	Bronze	Cu 84; Pb 1±; Sn 5; Zn 10
	Aluminium bronze	Cu (90-95); Al (5-10)
	Manganese bronze	Cu 70; Mn 30
	Gun metal	Cu 90; Sn 10
	Bell metal	Cu 75; Sn 25
	Dutch metal	Cu 80; Zn 20
	Copper coins	Cu 95; Sn 4; Zn 1
	5-cent piece	Cu 75; Ni 25
Iron Alloys	German silver	Cu (55-60); Zn 20; Ni (20-25)
	Steel	Fe (99-99.75); C (0.25-1)
	Nickel steel	Fe 94; C 1±; Ni 5±
	Chrome steel	Fe (94½-96½); C (1-1½); Cr (2½-4±)
	Tungsten steel	Fe 94; C 1±; W 5±
	Manganese steel	Fe 91; C 1±; Mn 8±
	Molybdenum steel	Fe (89-94); C 1±; Mo (5-10)
Lead-Tin Alloys	Solder	Pb (33-66); Sn (33-66)
	Pewter	Sn 75; Pb 25
	Shot metal	Pb 99; As 1±
	Type metal	Pb 75; Sb 20; Sn 5
	Britannia metal	Sn 85; Sb 10; Cu 5
Silver Alloys	Sterling silver	Ag 92.5; Cu 7.5
	Coin silver	Ag 90; Cu 10
Gold Alloys	U. S. gold coinage 21.6 k	Au 90; Cu 10
	18 k gold	Au 75; Cu 25
	14 k gold	Au 58.3; Cu 41.7
	10 k gold	Au 41.6; Cu 58.4
Fusible Alloys	Wood's metal (melts at 60.5° C.)	Bi 50; Pb 25; Cd 12.5; Sn 12.5
	Rose's metal (melts at 94° C.)	Bi 82; Pb 9; Sn 9
Miscellaneous Alloys	Babbitt's antifriction metal	Zn 69; Sn 19; Pb 5; As 4; Sb 3

X. COMPOSITION OF TERRESTRIAL MATTER TO A DEPTH OF 10 MILES

	SOLID CRUST OF EARTH, 93 PER CENT	OCEANS, 7 PER CENT	AVERAGE, INCLUDING ATMOSPHERE
Oxygen	47.17	85.79	49.85
Silicon	28.00		26.03
Aluminium	7.84		7.28
Iron	4.44		4.12
Calcium	3.42	.05	3.18
Magnesium	2.27	.14	2.11
Sodium	2.43	1.14	2.33
Potassium	2.49	.04	2.33
Hydrogen	.23	10.67	.97
Titanium	.44		.41
Carbon	.19	.002	.19
Chlorine	.06	2.07	.20
Bromine		.008	
Phosphorus	.11		.10
Sulphur	.11	.09	.10
Barium	.09		.09
Manganese	.08		.08
Strontium	.03		.03
Nitrogen			.03
Fluorine	.10		.10
All other elements	.50		.47
	100.00	100.00	100.00

The average density of the solid crust to a 10-mile depth is 2.6. The mean density of the ocean is 1.027. The average density of the whole earth is somewhat over 5. The average content of dissolved salts in ocean water is 3.5 per cent.

COMPOSITION OF OCEANIC SALTS

Sodium chloride, NaCl	77.76
Magnesium chloride, MgCl ₂	10.88
Magnesium sulphate, MgSO ₄	4.74
Calcium sulphate, CaSO ₄	3.60
Potassium sulphate, K ₂ SO ₄	2.46
Magnesium bromide, MgBr ₂	.22
Calcium carbonate, CaCO ₃	.34
	100.00

The above figures were calculated by F. W. Clarke and published in 1911 in Bulletin 491 of The United States Geological Survey entitled The Data of Geochemistry.

XI. — Logarithms

Nat. Number	0	1	2	3	4	5	6	7	8	9	PROPORTIONAL PARTS								
											1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	3	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	3	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	3	3	4	5	6	6	7
	0	1	2	3	4	5	6	7	8	9	PROPORTIONAL PARTS								
											1	2	3	4	5	6	7	8	9

XI. — Logarithms

Nat. Number	0	1	2	3	4	5	6	7	8	9	PROPORTIONAL PARTS								
											1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	4	5	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	4	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	4	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	4	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	4	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	4	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	4	4
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
											PROPORTIONAL PARTS								

XII. METRIC SYSTEM

The standard unit of the Metric System is the **meter**. It is a unit of length. Its multiples and submultiples are obtained decimally

10 millimeters (mm.)	= 1 centimeter (cm.)
10 cm.	= 1 decimeter (dm.)
10 dm.	= 1 meter (m.)

The unit of volume in the metric system is the **liter**. *It is the cubic decimeter.* Like the meter it is divided decimally.

$$\begin{array}{l} 1000 \text{ cu. cm. (c.c.)} \\ \text{or} \quad 1 \text{ cu. decimeter} \end{array} \Bigg\} = 1 \text{ liter}$$

The unit of weight is the **gram**. It is the weight of 1 c.c. of water at 4° C. It is divided decimally.

10 milligrams (mg.)	= 1 centigram (cg.)
10 cg.	= 1 decigram (dg.)
10 dg.	= 1 gram (g.)
1000 g.	= 1 kilogram (kg.)

XIII. TABLE OF EQUIVALENTS

Showing relation between some frequently used metric measures and their English equivalents.

1 meter	= 39.37 inches
1 centimeter	= .3937 inch
1 inch	= 2.54 centimeters
1 liter	= 1.0567 quarts
1 cubic centimeter	= .061 cubic inch
1 gram	= 15.43 grains
1 kilogram	= 2.2046 lb.
1 ounce	= 28.35 grams

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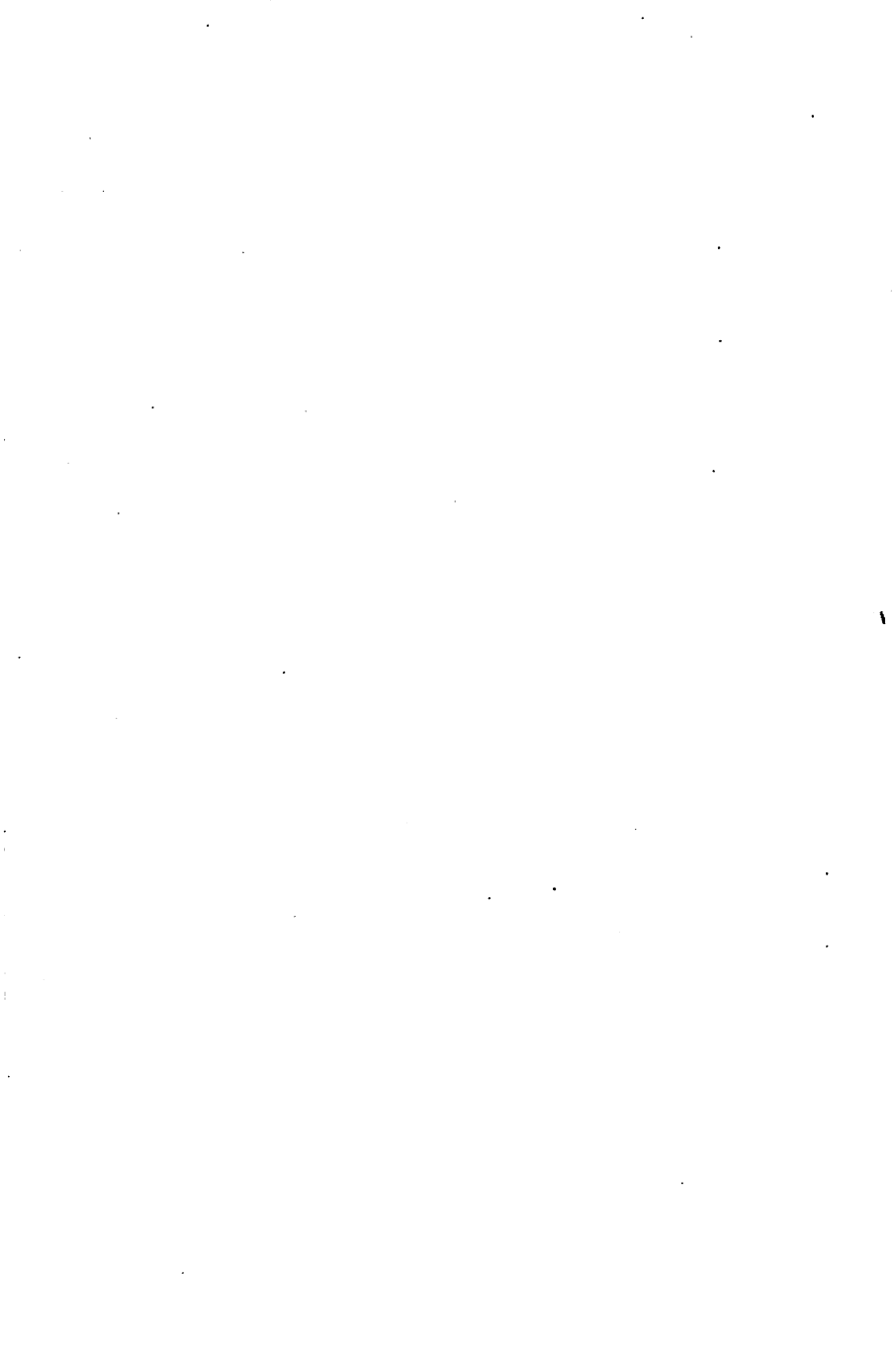
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O = 16

Aluminium	Al	27.1	Molybdenum	Mo	96.0
Antimony	Sb	120.2	Neodymium	Nd	144.3
Argon	A	39.88	Neon	Ne	20.2
Arsenic	As	74.96	Nickel	Ni	58.68
Barium	Ba	137.37	Niton (radium emanation) Nt		222.4
Beryllium	Be	9.1	Nitrogen	N	14.01
Bismuth	Bi	208.0	Osmium	Os	190.9
Boron	B	11.0	Oxygen	O	16.00
Bromine	Br	79.92	Palladium	Pd	106.7
Cadmium	Cd	112.40	Phosphorus	P	31.04
Cesium	Cs	132.81	Platinum	Pt	195.2
Calcium	Ca	40.07	Potassium	K	39.10
Carbon	C	12.00	Praseodymium	Pr	140.6
Cerium					140.6
Chlorine					35.4
Chromium					52.0
Cobalt					58.9
Columbium					94.0
Copper					63.5
Dysprosium					162.5
Erbium					167.3
Europium					152.0
Fluorine					18.9
Gadolinium					157.3
Gallium					70.0
Germanium					72.6
Gold					197.0
Helium					4.0
Holmium					164.0
Hydrogen					1.0
Indium					114.8
Iodine	I	126.92	Tin	Sn	118.7
Iridium	Ir	193.1	Titanium	Ti	48.1
Iron	Fe	55.84	Tungsten	W	184.0
Krypton	Kr	82.92	Uranium	U	238.5
Lanthanum	La	139.0	Vanadium	V	51.0
Lead	Pb	207.10	Xenon	Xe	130.2
Lithium	Li	6.94	Ytterbium (Neoytter- bium)	Yb	172.0
Lutecium	Lu	174.0	Yttrium	Yt	89.0
Magnesium	Mg	24.32	Zinc	Zn	65.37
Manganese	Mn	54.93	Zirconium	Zr	90.6
Mercury	Hg	200.6			

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